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CATALYTIC PROCESSES IN APPLIED CHEMISTRY

BY

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BEING VOLUME TWO OF A SERIES OF MONOGRAPHS ON APPLIED CHEMISTRY

Under the Editorship of

E. HOWARD TRIPP, Ph.D.

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EDITORIAL PREFACE

In these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date ; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place ; and to these many will add the growth of our sense of " values." The value of new work in science varies greatly : the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes : he must pick out the plums

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to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive ; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one ; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that " higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained."

E. Howard Tripp.

AUTHOR'S PREFACE

The applications of catalytic action in the chemical industries of the present day are so numerous that a very large volume, or even series of volumes, would be needed for a complete and detailed treatment of the whole subject ; again, there are not a few processes in which catalysis plays a minor, or sometimes an uncertain, part, which might or might not be deemed to be within the scope of a treatise on applied catalytic processes.

The enormous range and rapid extension of catalytic methods in industry involves a tendency towards over-specialisation on the part of those engaged in actual practice. It is of primary importance to maintain the broadest possible view of the whole subject, and the present volume has been written with this in mind, both as regards those who may already be well acquainted with one or more phases of catalyst technology, and those who may be concerned to apply catalytic action to manufacturing problems in which its aid has not previously been invoked.

The book is an attempt to give, within a reasonable space, a general account of how the principles of catalytic action are being applied in practice. Instances have therefore been selected for more detailed discussion, not necessarily because of the intrinsic importance of the products concerned, but mainly where it has appeared that the specific methods applied have a wider interest or are of potential application in other cases.

The specialist in any given branch of applied catalysis will, therefore, not expect to find more in the part of this book dealing with his own corner than he

already knows ; but it is hoped that in other portions of the work he may find matter which will assist him to bring new ideas to apply to the local problems which are his immediate concern.

The difficulties suggested in the first paragraph have been met, as far as possible, by referring to practically all the contemporary processes in which, so far as the writer is aware, catalysts are usefully employed (not forgetting the increasingly important developments in the use of " natural " catalysts (enzymes) in fermentation processes) ; but certain " borderland " topics such as the hydrogenation of coal (the *rôle* of catalysis in which, at the present stage of development, appears somewhat vague) or the technically important phenomena of anti-oxidants and autoxidation (which are definitely catalytic in nature, but are hardly, perhaps, applied catalytic processes) have been left over as distinctly outside the limits which the author has set himself.

The manifold instances available have been grouped, roughly, into firstly, the contact actions at solid surfaces which have been in general more thoroughly worked out than other types of catalysis, and perhaps are therefore more likely to stimulate further progress ; secondly, cases in which fermentation methods have been successfully applied ; and thirdly, the " homogeneous " actions of hydration, hydrolysis, esterification, dehydration, condensation, oxidation, etc., which are of high importance in technological organic chemistry, but which have not always been so thoroughly developed from a scientific standpoint as the more conventional and striking examples of " contact " processes.

It was felt desirable to preface the work with a short theoretical section, but theoretical principles have been considered, frankly, from their utility in guiding the practitioner ; for more general discussion of the fundamental aspects of catalysis the reader is recommended to one or other of the admirable books on this side of

the subject to which reference is made in the course of this volume.

It may be pointed out that, in order to economise space (since adequate illustration would have required a very large number of diagrams), as graphic description as possible has been attempted without recourse to pictorial illustration ; it may also be mentioned that all temperatures quoted in the book are given in degrees Centigrade.

Dr. E. Frankland Armstrong, F.R.S., Professor I. M. Heilbron and the editor of this Series have given the author the advantage of their criticism and advice during the preparation of the manuscript, for which his cordial thanks are recorded. He also expresses his grateful appreciation of the help rendered by Miss M. Tadman, M.Sc., whilst the book was in the press, especially in the matters of proof-reading and in compilation of the various indexes which, it was felt, were desirable in view of the somewhat heterogeneous mass of products, raw materials, and catalysts dealt with in the course of the work.

T. P. H.

University of Liverpool,
November, 1928.

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,, . .	Water-gas. .	Iron. . .	II.	2	78
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,, ,, .	Alcohol . .	Fermentation .	III.	3	264
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,, ,, .	Alcohol and acetic acid.	Sulphuric acid .	IV .	3	322
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Menthyl acetate .	Menthol . .	Anhydrous sodium acetate.	IV.	3	325
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Methylal . .	Formaldehyde .	Hydrogen chloride.	IV.	3	328
Methyl alcohol .	Water-gas. .	Zinc oxide, etc. .	II.	2	88
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Methyl benzoate.	Methyl alcohol and benzoic acid.	Sulphuric acid .	IV	3	324
Methyl cinnamate	Methyl alcohol and cinnamic acid.	Hydrogen chloride.	IV	3	325
Methylethyl ketone.	*iso*-Butyl alcohol	Copper . .	II.	7	181
Methylhexalins .	Cresols . .	Nickel . .	II.	9	229
Methyl salicylate	Methyl alcohol and salicylic acid.	Sulphuric acid .	IV.	3	324
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Urea. . .	Ammonia and carbon dioxide.	—	II.	3	116
Vulcanised rubber	Rubber and sulphur.	Organic bases; nitroso - compounds; substituted guanidines; thiourea derivatives: zinc or lead salts of complex thio-acids, etc.	IV.	4	344

CATALYTIC PROCESSES IN APPLIED CHEMISTRY

SECTION I

CHAPTER I

GENERAL DEVELOPMENT OF THE USE AND UNDERSTANDING OF CATALYTIC PROCESSES

ALTHOUGH catalytic changes were first so called by Berzelius[1] about the year 1835, they were recognised much earlier, and some of them were used in preparing chemical products several centuries before that date. Since, as we shall see, fermentation is also a case of catalytic action, it is obvious that catalysis has played an important (if unrecognised) part from the earliest times in the production of alcoholic liquors, and also of vinegar and some other simple commodities of this type. Of products which are more definitely in the category of "chemicals," the preparation of ether by the action of sulphuric acid on alcohol was familiar to the alchemists; sulphuric acid itself was made by the alchemists by combustion of a mixture of sulphur and nitre, and about 1740 Roebuck and others introduced the chamber process for manufacturing sulphuric acid, in which large amounts of sulphur dioxide were oxidised to sulphuric acid by the use of comparatively small proportions of oxides of nitrogen. At the commencement of the nineteenth century Clément and Désormes[2] and Sir Humphrey Davy, investigated the mechanism of this oxidation process, and showed in fact that the oxides of nitrogen had the functions of what we now term a catalyst.

Davy [3] also noticed a number of interesting chemical changes which were induced by the presence of heated platinum wire or sponge, such as the union of oxygen with hydrogen, volatile hydrocarbons, or alcohol. This marks one of the first scientific investigations in the realm of what is now known as heterogeneous catalysis, or catalysis at the surfaces of solids. He, with subsequent workers, also appreciated the poisoning or inhibiting action on the platinum of certain gases such as sulphuretted hydrogen and other gaseous sulphur compounds, ammonia, etc.

Somewhat later, but still prior to the Berzelian nomenclature of catalysis, Faraday [4] extended Davy's observations on platinum, developing, with characteristic genius, views, substantially unmodified even at the present day, upon the mechanism of contact action and the requisites for maintaining full activity in the contact material. Thus, in dealing with the ability of platinum to effect the union of hydrogen and oxygen, he sums up the practical points of the contact agent in the following sentence : " The only essential condition appears to be a perfectly clean and metallic surface, for whenever that is present the platina acts, whatever its form and condition in other respects may be ; and though variations in the latter points will very much affect the rapidity, and therefore the visible appearances and secondary effects of the action, that is, the ignition of the metal and the inflammation of the gases, they, even in their most favourable state, cannot produce any effect unless the condition of a clean, pure, metallic surface be also fulfilled."

He also expresses a general opinion as to the mechanism of these actions, which must be recognised as extraordinarily close in its main outlines to present-day views on the subject, namely, that catalytic action is conditioned by preliminary adsorption or incipient chemical combination between the interacting materials and a third agent (the catalyst) : " All the phenomena connected with this subject press upon my mind the

conviction that the effects in question are entirely incidental and of a secondary nature ; that they are dependent upon the natural conditions of gaseous elasticity combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all ; by which they are drawn into association mor or less close, without at the same time undergoing chemical combination though often assuming the condition of adhesion ; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction. I am myself prepared to admit (and probably many others are of the same opinion), both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance."

So that Faraday, who formulated these conclusions in 1833–1834, had clearly established in his own mind the general causes and effects of what is now termed heterogeneous catalysis.

As already stated, in 1835 Berzelius [1] surveying a number of chemical changes, the mechanism of which appeared difficult to understand in the light of then current explanations, suggested that such processes, which in many cases apparently proceeded in the presence of a specific agent but not in its absence, were due to the operation of what he called a catalytic force. He termed the particular agents which exhibited this force " catalysts," and held that the force in question was in some way a novel form or manifestation of chemical affinity. A few years later Liebig, discussing similar processes more or less from the standpoint of ferment action, put forward his vibration theory of catalysis, according to which a catalyst was simply in a state of molecular vibration which happened to

synchronise with, or at any rate be capable of communication to, other molecules, with the result that the latter were, so to speak, shaken to pieces, or in other words suffered decomposition. This vibration hypothesis did not survive the test of experiment and observation, whilst the catalytic force theory of Berzelius in its original form is more remote from the present-day conception of what goes on in catalytic action than Faraday's simple statement quoted above.

The academic classification and consideration of catalysis during the nineteenth century was somewhat confused, and may perhaps be passed over in the present book until we come to the modern theories as enunciated by Ostwald,[5] H. E. Armstrong,[6] and many others. These, to which we shall return a little later, were formerly of two distinct types, namely, those which relied on purely physical factors, and those which involved the assumption of the intermediate formation of something akin to definite chemical compounds; of late years these somewhat divergent views have more or less been reconciled or synthesised into the present adsorption or unstable intermediate-compound theory of the mechanism of catalysis.

We will revert for the moment, however, to what is the more immediate concern of this book, namely the development of the use of catalytic processes in industry during the past 150 years.

It is well, in view of the great advances which have been made in recent years in the theoretical understanding of catalysis, to get the facts concerning its industrial applications in approximately correct perspective. Dozens of catalytic processes were brought into use during the nineteenth century, some by pure empiricism, others by a combination of practical trials with such small fundamental knowledge as was then available, but in almost all these cases the inspiration may fairly be attributed to chemical intuition rather than to theoretical deduction. As in many other fields of applied physical chemistry, fundamental theory

until recent years lagged far behind practical applications ; and it is fair to enumerate some of the many instances in which contact action was successfully utilised on a technical scale without the advantage of the guidance of the laws of thermodynamics or, for example, of Ostwald's so-called criteria of catalysis. Thus, the production of sulphuric acid by passage of air and sulphur dioxide over platinum was patented in 1831, and the similar oxidation of ammonia to nitric acid was discovered in 1839, although it is true that in these cases efficient technical use of the methods had to await further information concerning the phenomenon of catalyst poisoning. On the other hand, the three processes of Weldon, Deacon and Weldon-Péchiney for the manufacture of chlorine were successfully worked out and practised on a very large scale from about 1860–1870 onwards, and in quite another direction the purification of coal gas from sulphuretted hydrogen by passage over iron oxide (which is essentially catalytic in nature), and the use of the Claus kiln in the Chance recovery process for the recovery of sulphur from alkali waste, have been carried on for very many years.

Turning to applied organic chemistry, the production of ether from alcohol by sulphuric acid was, it is true, made the subject of theoretical study by Williamson, Berthelot, and others, but in many other cases catalytic action was (and is) carried out on a technical scale more or less independently of theoretical considerations. It is only necessary to instance the manufacture of formaldehyde by passage of methyl alcohol and air over heated copper, the production of acetone by passage of acetic acid vapour over heated chalk, the many processes in which mineral acids are used to effect the addition of water to materials such as the more complex carbohydrates or the esters, and also to effect esterification of alcohols, or the use of metallic oxides in the autoclave processes for the hydrolysis of fats, to realise the large extent to which processes of

the more or less conventional catalytic type have been developed.

The variety of catalytic actions employed in the organic chemical industries, in cases which have not even yet been systematically studied from a fundamental point of view, is still more striking. The methods which the writer has in mind are those used in a wide variety of technical syntheses of coal-tar products, such as the employment of many different chlorinating agents and sulphonating agents and the use of numerous specific compounds to effect condensation of organic molecules, usually with elimination of the elements of water, hydrogen chloride, etc. In the latter category may be mentioned such compounds as aluminium chloride, sodium, alkaline hydroxides or ethoxides, etc., anhydrous or aqueous solutions of mineral acids of varying concentrations, and, for example, the use of sodium acetate or zinc chloride as an aid to acetylation.

The above statement is intended not so much to belaud empiricism (although the technical results obtained in spite of lack of theoretical guidance merit commendation) as to indicate the need for systematic academic study of these less understood examples of industrial catalysis ; for it is not unreasonable to predict that treatment of these methods on similar lines to that which has been so successfully applied to, for example, the modern synthetic ammonia, methyl alcohol, and other industries could not fail to be eminently fruitful.

Coming to the main advantages of the use of catalysts in technical methods, and without precisely defining the term " catalyst " until a little later, it is evident that the chief object to be gained is the elimination of the use of accessory chemicals. Since the latter react in equivalent proportions, it is, of course, obvious that, in addition to their consumption in amounts corresponding to the output of the desired product, there is also the concurrent formation of an equivalent amount

of by-products which very frequently are of little value, or at least require considerable further treatment before they acquire an adequate market value. Under ideal conditions (and it may be borne in mind that the ideal is often quite reasonably approachable) a catalyst can often be found which will induce a desired chemical reaction with the formation of very few by-products of a useless nature, and which is capable of effecting the transformation of many times its own weight of interacting material.

The actual amount so transformed in practice varies widely. In some of the organic chemical processes in which the catalyst itself is apt to become altered by side reactions, the amount may only be of the order of say 50–100 times the weight of catalyst present; at the other extreme we have instances such as the use of platinum gauze in the oxidation of ammonia, where with suitable precautions the life of the catalyst is practically indefinite and the rate of transformation exceedingly great (thus a piece of platinum gauze 6 in. by 4 in. is capable of producing about 12 lb. of nitric acid per hour). Broadly speaking, then, the first economic objective of a technical catalytic process is the elimination, or reduction to a minimum, of the use of accessory chemicals.

There is another aspect to be considered, namely, the economy of energy as well as of material. The conventional forms of catalyst sometimes lead to economy in both directions—that is to say, whilst avoiding the use of additonal chemicals a reaction may also be carried out at, for example, a much lower temperature than would be possible in the absence of a catalyst, or a process may become possible which, in the absence of a catalyst, requires the application of considerable actinic (photo-chemical) or electrical energy, etc. On the other hand, many of the modern processes of catalysis involve the use of extraordinarily high pressures and, in some cases, high temperatures—in other words, the consumption of considerable energy

in the form of power and heat. Many of the latter type are proving very successful in technical practice, but this should not entirely blind us to the fact that we have at command a whole range of natural catalysts which operate at or close to the ordinary temperature, in some cases with exceedingly great efficiency, if we only knew how to use them.

The investigation and utilisation of the enzymes produced by living organisms is a field of industrial research which, up to the present, has received little systematic investigation. It is, of course, impossible to expect that anything but a proportion of the variety of chemical products required by modern civilisation can be prepared by processes of the nature of fermentation ; but it is equally certain that far more use could be made of enzyme action in industry in many directions, for enzyme action is often closely connected with hydrolysis and also with the reverse action of condensation or dehydration, and it is further capable, in specific cases, of effecting oxidation or reduction ; the elaboration of nitrogen compounds by enzyme action is another region in which there obviously may be possibilities. As already stated, enzyme actions proceed under the ordinary conditions of temperature and pressure, and the prospect, even if remote, of combining economy in fuel costs with that of accessory chemicals is sufficiently attractive to invite more intensive study of this field.

For these reasons certain processes of fermentation or enzyme action which are already in use for the production of specific chemical products have been treated in appropriate sequence in this book as instances of applied catalysis. The examples at present available (with the exception of alcohol, acetic and lactic acids, acetone and butyl alcohol) are neither numerous nor, perhaps, relatively important ; it is, however, well to stress the point that these processes are fundamentally of the same nature as the more ordinary forms of catalytic action, and, although the biochemical

technique involved is of course quite different in many aspects from the manipulation necessary in the cases of ordinary chemical contact agents, the fundamental action in both cases is at present understood to be of the same nature. Thus, from both a theoretical and a practical point of view, it is most desirable to bring fermentation processes into line with the more conventional technical catalytic methods.

We may now return to a brief survey of the general development of theoretical views of catalytic action during the past thirty to forty years. In the first place we may refer to the restatement of the earlier views of Berzelius, Liebig, etc., on catalysis by Ostwald in 1888; he laid down a series of " criteria " of catalysis, the most important of which was the definition that " catalysts are substances which change the velocity of a given chemical reaction without modification of the energy factors of the reaction."

It is by no means agreed, however, that a catalyst can only alter the speed of a chemical reaction which would take place (possibly exceedingly slowly) in any case ; the view has been maintained consistently by various workers throughout the development of catalytic theory that a catalyst can actually initiate a chemical change, that is to say, can cause an action to occur which in its absence would definitely not proceed. (Of course, this case can be included in Ostwald's criteria by saying that such chemical changes proceed only at infinitely slow speeds in the absence of a catalyst ; but this is tantamount, for all practical purposes, to accepting the statement that a catalyst can cause a chemical change to take place which otherwise would not occur.)

At the same time it is equally clear that no catalyst can operate against the fundamental laws of thermodynamics. The present knowledge of the application of these laws enables, in many cases, data as to the equilibria or thermal conditions of chemical changes to be determined from a perfectly general point of view ;

and, if the appropriate physical and chemical constants of the particular interacting compounds which are required in these calculations are known with sufficient accuracy, it becomes possible to state whether a given chemical reaction is thermodynamically possible or not, quite independently of the intervention of any catalyst. Given energy conditions which allow a certain reaction to take place, two cases arise : the action may not proceed with measurable speed in the absence of a catalyst, or it may take place at any particular rate. In either case the presence of appropriate compounds may cause a marked alteration in the progress of the reaction in question ; it may cause the change to proceed at a useful speed where otherwise it could not be carried out at all, it may accelerate a slow reaction, or, on the other hand, it may induce a retardation of the normal rate of action (" negative catalysis ").

From the point of view of the technologist it seems more useful to define a catalyst as a substance which alters the speed of reaction (including the case of apparent initiation of reaction), but which remains unaltered in chemical composition after the chemical change is completed. This definition covers a number of cases which we shall encounter in which the physical state of the catalyst may undergo alteration as the main reaction proceeds, whilst it also emphasises the important factor that, if the catalyst itself is chemically changed by side-reactions (catalyst poisoning), it is no longer able to function as a catalyst and the main reaction tends to revert towards its normal, non-catalysed rate of progress.

Catalytic action is at present recognised, so far as chemical affinity is concerned, to proceed in accordance with the same natural laws which operate in any other chemical change. The energy changes taking place in a catalysed system, and the way in which the catalyst transfers, or continuously acquires, the energy necessary to enable the chemical change to proceed, are not so clearly defined at present as the purely chemical side

of the question ; but, on the other hand, this state of affairs is not peculiar to catalysis, for our lack of understanding of the precise energy relations during chemical change extends to a large number of reactions of many kinds.

Chemically speaking, catalytic changes proceed, as already stated, according to the laws of thermodynamics, and consequently follow the general principles of chemical kinetics and of the law of mass action ; but, as will be explained in the next chapter, it is necessary to have an explicit knowledge of the local conditions in a catalytic system in order to understand the specific application of the law of mass action in particular cases.

The modern developments of catalytic theory are the result of a very large quantity of experimental observations which have been carried out by numerous groups of workers in many countries ; they have undoubtedly led to the elucidation of much that was formerly puzzling and at one time more or less shrouded in a prudent veil of mystery, and the reader who is interested in the detailed theory of this most fascinating branch of chemistry will do well to consult some of the recent monographs dealing more exclusively with this side of the subject, such as Rideal and Taylor's "Catalysis in Theory and Practice," Falk's "Catalytic Action," the Reports of the American Committee on Contact Catalysis, and Sabatier's "La Catalyse en Chimie organique."

The present book, in its attempt to give a systematic survey of the industrial applications of catalysis, is likewise concerned with the fundamental theory upon which the technical science depends ; but it is only possible to offer in as condensed a form as possible a summary of the present state of knowledge and general opinion.

Academically there has always been a tendency to divide catalytic actions into the obvious categories of those which take place in a homogeneous system and

those which are heterogeneous (that is to say, broadly, those in which a solid catalyst effects chemical change in a liquid, liquid and gaseous, or gaseous system). It is usually the custom to discuss the apparently simpler case of homogeneous catalysis before proceeding to that in heterogeneous systems, but the trend of recent work has been so much in the direction of better understanding of heterogeneous contact actions that it seems quite possible that (at all events in the case of a condensed summary) a clearer conception of the subject will be arrived at by taking the heterogeneous class first.

The next chapter is therefore devoted to an outline of present-day views on contact action at solid surfaces and is followed by a chapter on the theoretical aspects of enzyme action, which is closely related to the previous case. A chapter on homogeneous catalysis follows, and it may be said here that, although this field was, until recently, probably more thoroughly explored than actions at solid surfaces, and the general conditions governing the rate of reaction, etc., were fairly well understood, the actual mechanism by which a catalyst operates in a homogeneous system is not yet so clear as in the other case, and the knowledge gained from the study of heterogeneous actions may well afford insight into the precise function of catalysts in homogeneous systems.

Classification of Industrial Catalytic Processes.

The formal orientation of catalytic actions into homogeneous and heterogeneous divisions is more or less essential for consideration of the theory of this branch of chemistry, and it also serves as the most suitable basis for grouping the manifold industrial applications of contact action. The remaining Sections of this book are concerned with technical processes, which, broadly speaking, may be classified as catalyses at solid surfaces, fermentation methods, or catalyses in homogeneous systems ; they thus correspond in some

measure with the theoretical aspects which are referred to in Chapters II, III, and IV of this Section.

The order of treatment has been determined by several considerations. The heterogeneous actions, or catalyses induced by solid surfaces, are the most numerous class, and also include many of the most important instances of industrial catalysis, both from the standpoint of output and also from that of the intrinsic value of the products to the community; consequently they have been given pride of place.

The following Section (III.) is devoted to a short survey of technical processes which are governed by enzyme action. This procedure, which involves a break in the logical treatment of the purely chemical methods, is intended to focus attention on two points: (i.) these biochemical catalyses are intermediate in character between the heterogeneous and homogeneous systems of purely chemical catalysis, since they are surface actions which frequently take place in an apparently homogeneous medium; and (ii.), more important, they are processes which are not only catalytic (*i.e.*, avoid the use of extra chemical reagents), but also proceed at or near to the ordinary temperature, with consequent large economy in fuel costs. Emphasis has already been laid (p. 8) on the desirability of exploring biochemical methods of chemical change wherever possible, in order to arrive at manufacturing processes which combine elimination of auxiliary chemicals with economy in heat energy. It is, of course, unreasonable to expect that ordinary technical chemical methods will be superseded eventually by controlled enzyme action, but the growing list of chemical compounds manufactured by fermentation processes indicates that this branch of applied catalysis is worthy of continued and intensive investigation, and that in many specific instances its employment may be expected to receive considerable extension.

Section IV. deals with catalytic actions which proceed in a homogeneous (liquid) system, a category

which includes many important technical processes, both old and new. It is not so diffuse in general method, and does not contain so many instances of huge outputs of heavy chemicals, as the heterogeneous section ; but it embraces many technical methods of hydration, dehydration, and esterification (including the production of ether, glucose, acetic acid, esters, etc.), as well as various other kinds of chemical change.

The treatment of technical catalytic actions according to their general character in this way has, it is felt, conferred a certain amount of order upon the general scheme of the book. At the same time, readers interested in the manufacture of a particular chemical may wish to be directed more immediately to the pages in which its catalytic production is discussed. The chief processes mentioned in this book have therefore been tabulated (pp. xi–xiii, following the Table of Contents), first, in the order in which they are treated, and, secondly, with primary reference to the product of manufacture in each case.

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Chapter I

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CHAPTER II

THEORETICAL ASPECTS OF CATALYSIS AT SOLID SURFACES

UNTIL about 1920–1925 there was a distinct conflict of opinion as to the mechanism by which a solid catalyst effected chemical change in gases or liquids; the rival views may be referred to briefly as the physical and the chemical (or intermediate-compound) theories of heterogeneous catalysis.

Physical explanations of catalysis were first based on the fact that porous materials (*e.g.*, platinum or charcoal), which accelerated such actions as the union of hydrogen and oxygen, possessed the capacity for concentrating gases in a layer at their surfaces, with accompanying thermal effects similar to those observed in the liquefaction of a gas. It was therefore concluded by van't Hoff [1] that the gases were brought into a state of compression and abnormal concentration by the catalyst, with the result that chemical action was enormously accelerated without any direct chemical intervention of the catalyst. At this period the gaseous concentration or adsorption was regarded as a "diffusion layer" [2] several molecules thick, at the solid surface, the rate of chemical interaction being a supposed function of the rate of diffusion in this layer, and not depending on any actual chemical change at the surface of the catalyst.

As Sabatier [3] has emphasised by two clear-cut examples, this view fails to account for varying chemical action exerted on one and the same substance by different materials: isobutyl alcohol, which when passed over copper at 300° yields isobutyl aldehyde and hydrogen, by passage over alumina at the same temperature gives isobutylene and water, and over uranium oxide at the same temperature a mixture of

all four substances. More striking still, formic acid is decomposed by one oxide, that of zinc, into hydrogen and carbon dioxide, and by another (titania) exclusively into carbon monoxide and water. A more recent instance of exactly the same kind is the combination of carbon monoxide and hydrogen in presence of different materials; with nickel, methane is formed almost exclusively, with zinc oxide or chromate, quantitative yields of methyl alcohol can be obtained, whilst with an iron-alkali catalyst a mixture of higher alcohols, ketones, and hydrocarbons is formed.

Similarly, purely physical theories of this type fail to account for a phenomenon which is often met with, namely, the markedly selective action of many catalysts together with their power of producing isomeric or other change, which, as will be shown a little later (p. 19), is absolutely clear evidence that chemical inter-relationship of an intimate nature has occurred between catalyst and organic molecule.

On the other hand, the investigations of the late Lord Rayleigh,[4] Sir W. B. Hardy,[5] Irving Langmuir,[6] and others defined more clearly the physical nature of adsorption, and have shown that, whilst a "diffusion layer" of adsorbed molecules may exist in many cases, the primary condition of adsorption of a gas at a solid surface is due to a single layer of molecules which (according to Langmuir) are held at the surface by a force which is indistinguishable in effect from chemical force or affinity. In this form the physical or adsorption theory of catalysis, which has been closely studied in recent years by a number of workers, including especially the members of the physico-chemical department of the University of Princeton, U.S.A., approaches very close to the corresponding development of the older "intermediate-compound" view of advocates of chemical theories of catalysis.

A chemical or "intermediate-compound" theory of catalysis was first put forward by de la Rive and Marcet[7] in 1828, and was considerably elaborated by

Berthelot[8] in 1880, in connection with the catalytic decomposition of hydrogen peroxide. It was restated by H. E. Armstrong[9] who regarded a catalyst as completing, with the interacting compounds, a closed voltaic circuit; this view affords an explanation of catalysis in keeping with the general theorem that chemical action is reversed electrolysis.

Williamson's investigations[10] of the dehydration of alcohol by sulphuric acid and Squibb's work[11] on the conversion of acetic acid into acetone by passage over barium carbonate are examples of catalysis in which the intermediate compounds between catalyst and organic compound (ethyl hydrogen sulphate or calcium acetate) are capable of isolation. Sabatier[3] explained the dehydrating action of such oxides as alumina or thoria on alcohols and organic acids on strictly analogous lines, and proceeded to the case of hydrogenation of organic compounds over reduced metals; but here he abandoned the conception of complex formation between organic compound and metal, and only considered the possibility of union of hydrogen with the metal.

After the striking development of the technical process of fat hydrogenation from about 1910 onwards considerable attention was paid to the mechanism of catalytic hydrogenation in liquid systems. Although previous workers (including Fokin,[12] Moore, Richter and van Arsdel,[13] Thomas[14] and others) had observed an approximation to action at a unimolecular or logarithmic rate in liquid hydrogenation, Armstrong and Hilditch[15] showed that working with rigorously purified liquids and gases, and under conditions favouring maximum contact of all the components of the system, equal amounts of unsaturated compound were hydrogenated in equal times at any stage of the process, the action being of the "nul-molecular" order. It was also shown how linear curves could be transformed into unimolecular curves, (i.) by the presence of a substance which slowly combines with the catalyst to form a permanent compound (catalyst

poisoning), or (ii.) by the accumulation of gaseous impurities in the gas-space above the acting system (thereby altering the otherwise constant concentration of hydrogen above the liquid).

Moore[16] found that during hydrogenation of esters of oleic acid, isomeric elaidic and iso-oleic acids (in the latter of which a double bond has been displaced along the carbon chain) were produced in addition to ethyl stearate. This is further proof of the direct chemical connection between the reacting organic compound and the contact agent. Similarly, hydrogen can be transferred under suitable conditions from a saturated to a less saturated molecule in presence of a catalyst, so that catalytic hydrogenation and dehydrogenation can proceed simultaneously in a system comprising only two liquid organic compounds and an appropriate contact agent.

Armstrong and Hilditch[15] therefore regarded hydrogenation at the surface of a catalyst as explained by primary interaction between catalyst and unsaturated compound (an action produced by chemical forces, but not necessarily giving a stable, isolable compound), the complex so formed being decomposed by hydrogen, also regarded as coupled with the nickel (both hydrogen and unsaturated compound being considered as having some affinity for the nickel) :—

$$-CH{=}CH- + Ni + H_2 \rightleftharpoons (-CH{=}CH-, Ni, H_2)$$
$$\rightleftharpoons (-CH_2{-}CH_2-, Ni) \rightleftharpoons Ni + -CH_2\,.\,CH_2-$$

Perhaps the most striking illustration of the close chemical connection between the interacting organic compound and solid catalyst is afforded by the phenomenon of selective hydrogenation, that is, the preferential attachment of hydrogen in presence of a catalyst to one of two or more centres of hydrogenation. When it occurs, hydrogenation of all the unsaturated groups present is effected eventually, but the process is consecutive, and, except to a minor extent, the unsaturated groups are not attacked concurrently.

It has become apparent that selective hydrogenation is a general rule rather than an exceptional occurrence.

It was first observed by Vavon[17] and by Paal[18] in 1911–1912 in the hydrogenation of compounds such as limonene, carvone and the like. It has been observed by numerous workers in the case of various unsaturated fats and fatty acid esters; in these instances it may be said that all derivatives less saturated than oleic acid esters are reduced to the latter condition before appreciable amounts of oleic acid compounds are converted to the corresponding stearic acid esters. Parallel with these it is found that the rate of hydrogenation, measured by plotting absorption of hydrogen against time, gives a series of approximately linear curves, with a well-marked discontinuity in the region which corresponds to complete formation of monoethylenic derivatives from the less saturated compounds. The same variation in rate is observable in the case of terpene and other compounds; but it should be noted that selective hydrogenation cannot be explained by variation in the rate of addition of hydrogen to different unsaturated groups, because, although the rate of hydrogen absorption is in general constant during each stage of the process, the relative rates often are not widely different. Therefore, the selective process, which is almost quantitative in nature, cannot be ascribed to the mere effects of relative concentration and affinity, according to the simple operation of the law of mass action. Finally, it should be mentioned that the course of selective hydrogenation is not decided simply by the relative degree of unsaturation of the molecule, but also depends on other factors, such as the contiguity of oxygenated groups to the unsaturated centres, and also (as has been illustrated by Lebedev, Kobliansky and Yakubchik[19]) very definitely by the degree of substitution at the carbon atoms which form the ethylenic linkages.

All these subsidiary phenomena are clear proof that organic compounds, equally with hydrogen or other simple inorganic materials, enter into definite chemical

relationship with solid catalysts, although it is comparatively rare to encounter instances in which stable intermediate compounds between catalyst and interactant can be isolated. As we shall see a little later, it is probably essential, in order that catalytic action may proceed, that the intermediate or adsorption complexes so produced should be suitably unstable, and the nearest approach to an equation expressing the progress of catalytic change is probably something on the lines of that given above.

In this form the " intermediate-compound theory " coincides in most respects with the physicists' " unimolecular layer " adsorption theory, and from this point the development of the general modern view of catalytic action can best be dealt with on the basis of the unified views : for the physicists have come to the conclusion that the adsorption processes concerned in catalysis are conditioned by forces indistinguishable from chemical affinity and are mainly concerned with unimolecular layers, whilst at the same time chemists have come to appreciate that an association of the organic molecules with the solid catalyst occurs which is at least equal in general character to, for example, the association between hydrogen and a catalyst.

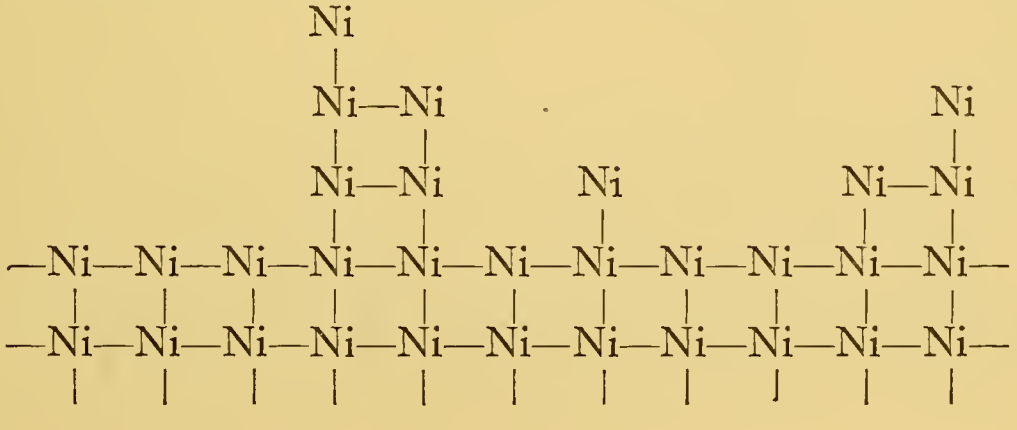
H. S. Taylor and Burns [20] showed that ethylene, carbon monoxide, or carbon dioxide is adsorbed by active (but not by inactive) metallic catalysts, *e.g.*, nickel or copper, to an extent which is of the same order as that of hydrogen, and far greater than that of inert gases such as helium or nitrogen. Beebe and Taylor [20] established that the heats of adsorption of hydrogen, ethylene, or carbon monoxide on catalytic nickel and copper varied from 13,500 to 20,500 calories (depending on the past history of the adsorbent). These magnitudes are comparable with those obtaining for mild chemical actions rather than for physical condensations or change of state (*ca.* 450 calories), and may be taken as a final proof of the general theorem that the association between inter-

acting compounds and metal catalyst is definitely chemical in type.

These workers have also shown that a catalyst, prepared at a low temperature and capable of adsorbing a definite amount of interactant, adsorbs less of the latter after exposure to a somewhat higher temperature, and progressively less and less after heat treatments at successively higher temperatures, thus suggesting that an action analogous to sintering takes place with resulting diminution in the number of exposed points in the catalyst surface; this evidence is complementary with the data which Armstrong and Hilditch [25] collected (*v. infra*) as to the relation between bulk gravity, exposure to high temperatures, and activity of unsupported nickel catalysts.

Taylor [21] has brought all the foregoing observations on rate of hydrogenation, adsorption capacity of catalysts, thermal adsorption data, behaviour of catalysts to heat and " poisons," etc., within the scope of a more detailed conception of the atomic condition of an active catalyst, which is briefly as follows :—

The X-ray examination of metallic hydrogenating catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material. This does not exclude the occurrence, however, of local excrescences or irregular formation of atoms at the crystal surface, and he has suggested that the structure of a typical catalyst surface may be somewhat as indicated in the diagram, atoms being thrust irregularly at various points above the normal surface of the metal :—



The points at which isolated or semi-isolated nickel atoms are supposed to be situated are, according to this view, the seat of catalytic activity. This picture affords an adequate explanation of such matters as :—

(i.) The importance of irregular surface in general ;

(ii.) The sensitiveness of an unsupported metal catalyst to increases of temperature which would increase the inter-atomic vibration sufficiently to cause the isolated atoms to take up more stable positions in the plane surface (a " sintering " effect far removed from any incipient liquefaction of the metal).

(iii.) The action of catalyst poisons and probably of some catalyst promoters ;

(iv.) The possibility of interaction with other molecules owing to the affinities of the exposed atoms being less saturated by neighbouring nickel atoms, and consequently making these atoms more " unsaturated " or active and inclined to enter into chemical relation with other molecules.

There is some evidence, although it can hardly be regarded as conclusive, which indicates that at the moment of actual catalytic action the active atoms in Taylor's theory may be actually detached from the surface, thus attaining to a state in which a definite " intermediate-complex " of an atom of catalyst and the interactants has a momentary existence. This view, if not essential to the theoretical explanation of the catalytic process, is further compatible with the approximation of such exposed atoms to the " gaseous " state in their thermal behaviour during adsorption, and with the observation of Hulett and Berger [22] on the minute but definite loss in weight of platinum when heated in oxygen.

The relation between hydrogen pressure and the rate of hydrogenation of a variety of liquid compounds, which is linear for simple types of ethylenic compounds, but varies from the direct relationship when active groups such as hydroxyl or carboxyl are present in the molecule or when gaseous " toxic " compounds such

as carbon monoxide are present in the hydrogen used, has been dealt with by Armstrong and Hilditch,[23] and shown to be fully in accord with the observations of Taylor and the Princeton school on the preferential adsorption of many organic compounds by catalysts, and with the above theoretical views.

This conception of the catalyst surface may also be considered in conjunction with selective action, and it may be hazarded that, for example, during selective hydrogenation that ethylenic centre which is preferentially saturated is probably *not* the one which is most strongly held at the nickel surface. The more strongly adsorbed of two unsaturated groups is probably less prone to saturation; chemical change would then tend to occur at the weaker attachment between the remaining double bond and (presumably) some other exposed nickel atom at the surface. The recent observation of Pelly,[24] that in a mixture of neutral fat and free fatty acid the free fatty acids are hydrogenated preferentially to the neutral fat, reinforces this view. It is generally agreed that the carboxyl group of an organic acid has a strong attraction for catalytic nickel, and it thus appears that those molecules which are, so to speak, anchored at the nickel surface by the free acidic radicle are in a position to undergo saturation of the double bond more readily than are neutral esters.

In order to illustrate the general mechanism of catalytic action at a solid surface concisely and rapidly, the work of the Princeton school, and of a few other investigators who have studied more particularly the phenomena of hydrogenation, has been dwelt upon in some detail. It should, however, be stated that many other workers have contributed towards the present knowledge of this branch of theory, including Constable, Hinshelwood, Rideal, Bancroft, Adams and co-workers, etc., etc.

The outstanding change which has taken place as a result of the extended studies of the past few years on

the processes of catalysis is that the catalyst is now looked upon, not in the mass, but with respect to certain select atoms in the mass in which all the activity displayed is now believed to reside. In Taylor's words, " this picture supplies a reason for much of the mystery with which the subject of contact catalysis has been surrounded hitherto. For it shows that the properties of the contact agent are to be differentiated from the bulk properties of the substance of which the catalyst is composed ; that it is rather the properties of the individual atoms or molecules of the catalyst, with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change." It follows, therefore, that the worker on heterogeneous catalysis is in the somewhat unique position of observing the behaviour of a selected few of the atoms or molecules present in the material under investigation, instead of dealing with the average behaviour of the whole assemblage of an enormous number of ultimate particles.

The recent work helps to emphasise the essential conditions of suitable surface which must obtain before any catalysis occurs : when a suitable surface is present, no catalytic action will occur unless on that surface (whether deposited or forming the total surface *per se*) there is a specific chemical adapted to adsorb or form appropriate intermediate compounds with the interactants ; for example, if hydrogen and ethylene are presented to such a surface no formation of ethane will occur unless there is present some specific material such as palladium, platinum, nickel or copper.

Essential Conditions of the Catalytic Surface in Practice.

The principles on which depend the practical formation and maintenance of an active catalyst surface become fairly obvious when approached from the standpoint of the preceding statement. Since catalysis is largely dependent on the surface at which the action

takes place, it may be expected that colloidal sols would be the most active catalysts ; this, however, is not so, owing to the liability of the sol form to be affected by extraneous matter. Nevertheless, certain other colloidal materials (*e.g.*, gum arabic) have a stabilising or " protective " effect on the activity of a colloidal sol catalyst, although the protective colloid has also the effect of reducing the initial maximum activity of the sol.

In the case of solid surfaces somewhat similar phenomena are met with. Thus, confining ourselves again, by way of example, to the case of nickel, the finely divided metal *per se* is extremely sensitive to the influence of temperature ; something akin to sintering takes place, the apparent volume of the metal is reduced and also the adsorption capacity for ethylene, hydrogen, etc. Evidently the exposed nickel atoms (in terms of the above conception) are readily, so to speak, shaken down by relatively mild exposure to heat, so that a less irregular surface results with fewer centres of catalytic activity.

If, however, the nickel has been prepared by deposition as carbonate on an inert porous support (especially kieselguhr, or charcoal), an effect is obtained which is somewhat similar to that of a protective organic colloid on a catalyst sol, namely, the reduced supported nickel is able to withstand much higher temperatures than the unsupported catalyst without any serious alteration in activity ; but, contrary to the case of the protective colloidal sols, the initial activity of the supported nickel is usually far greater than that of a corresponding mass of unsupported nickel. Exposed nickel atoms in a supported catalyst may well be separated from each other to some extent by intervening molecules of the irreducible support, so that the cohesive effect between the metal particles as a result of heat is much less pronounced.

These statements may be illustrated very briefly by the data in the following tables, which show : (i.) some relations between temperature treatment, apparent

volume, and catalytic activity of various nickel preparations (Armstrong and Hilditch [25]), (ii.) the adsorption capacity for hydrogen of copper and nickel catalysts prepared at varying temperatures (Pease, Beebe and Taylor [26]), (iii.) the activity of a supported nickel catalyst with varying proportions of the nickel in a reduced condition (Armstrong and Hilditch [25]).

Table I

	Source of Reduced Nickel.			Reduced Nickel.			
	Sp. Gr.	Bulk Gr.	Temperature of Reduction.	Sp. Gr.	Bulk Gr.	Pyrophoric character.	Catalytic Activity.
		c.c.			c.c.		
Powdered fused nickel oxide.	6·96	0·35	500°	8·14	0·52	None	None
Precipitated nickel hydroxide.	5·41	0·87	300°	7·85	0·83	Pronounced.	(*a*)
			500°	8·18	0·56	Medium	(*b*)
Corresponding oxide.	3·04	0·91	300°			Faint	(*a*)
			500°			None	(*b*)
Nickel oxide on diatomaceous earth.	1·63	3·22	500°	1·85	2·67	None	Very active

(*a*) Fairly active ; in vapour hydrogenation this type of nickel is capable of hydrogenating the benzene ring.

(*b*) Very little activity ; catalysts reduced at a lower temperature but above 300° are intermediate in activity between (*a*) and (*b*), and perform easy hydrogenations such as the saturation of a simple ethylenic linkage but fail to attack the aromatic nucleus.

Table II (Pease, Beebe and Taylor)

Catalyst.	Heat Treatment.	Adsorption of Hydrogen at 0° and 760 mm.
A. 100 gm. active Cu .	No heat beyond reduction of oxide at 200° . .	3·70 c.c.
B.	"A" heated to 450° for 1·5 hours . . .	1·15 ,,
C. 27 gm. active Ni .	Obtained by reduction of oxide at 300° . .	35 ,,
D.	"C" heated at 400° for 4 hours . . .	16 ,,

Table III

Nickel oxide deposited on diatomaceous earth, and containing a total concentration of 14·5 per cent. of nickel, was reduced in hydrogen at 450°–500° to varying extents. The relative activities of the products were measured roughly by the rate of absorption of hydrogen when linseed oil was hydrogenated at 180° with an amount of the catalyst such that the total nickel present was 0·1 per cent. of the oil; the following results were obtained :—

Per cent. Reduced Nickel.	Ratio of Reduced : Total Nickel.	Catalytic Activity.	
		H_2 Absorption Litres p. min.	Ratio. (Most Active Catalyst as Unity).
2·88	0·199	0·130	0·280
3·56	0·246	0·159	0·342
5·63	0·389	0·302	0·649
6·45	0·445	0·333	0·716
8·46	0·583	0·456	0·981
10·36	0·714	0·465	1·000
12·05	0·886	0·465	1·000
14·19	0·979	0·445	0·957

It is considered that figures of this nature indicate that the activity of a catalyst is dominated by the condition of the surface layer of reduced nickel, since it is obviously this part of the catalyst mass which will be first reduced in hydrogen to the metallic state.

The covering of the support with nickel compound appears to resemble the application of soapy water to a sponge; the latter will soak up a large amount of water, but it is only that at the external surface which is immediately efficient for washing.

The use of supported catalysts is fairly widespread and will be referred to again from a more technical point of view at various points throughout Section II of this book. The above is intended to give a theoretical outline of the practical conditions governing active catalyst surfaces, and should be taken in conjunction with the subsequent part of the present chapter which deals with the theory of catalyst promoters (pp. 32–38).

Catalyst Poisons.

Some catalyst " poisons " (*e.g.*, hydrogen sulphide, or acids), may act by definitely and chemically changing the catalytic metal, although the amount of a very toxic substance necessary to suppress the activity completely is far less than that required to combine in stoichiometrical proportion with the metal. Many other substances, however, exert a paralysing effect on the activity by covering up the catalytic surface and preventing contact between the metal and the other interactants. Thus Sabatier has pointed out that in a vapour hydrogenation process the merest film of condensed organic vapour on the catalyst is sufficient to stop all further hydrogenation.

Again, in liquid hydrogenation, especially in technical processes such as fat-hardening, where the materials to be treated are not pure chemical compounds, it frequently happens that impurities of a colloidal nature are present which are partially coagulated by the action of heat; such substances (resins, tars, mucilaginous matter, etc.), are naturally deposited on the solid catalytic material, and, whether chemically harmful or not to the metal, hinder the process by preventing proper contact.

In other cases, of which the " poisoning " action of carbon monoxide on nickel is a well-known example, the effect is not permanent and the activity is restored when the impurity has been displaced from the interacting system.

The picture of the mechanism of catalytic action afforded by the most recent theories on the subject (pp. 21–23) again helps considerably to an understanding of what goes on when a catalyst is " poisoned " or its activity is lessened by the presence of an added substance.

Catalyst " poisoning " is undoubtedly always due in the first place to the same factor, which precedes chemical change, namely, the formation of a unimolecular adsorption layer or unstable compound at the solid surface.

If the adsorbed material is a colloidal suspension or a liquid or solid such as resins, tars, etc., contact with the other interacting substances will be prevented. If the adsorbed material has a pronounced chemical action on the surface owing to the production of a sulphide or other salt, the character of the surface is permanently altered and the catalyst destroyed; the reason that minute proportions of a strong "poison" such as hydrogen sulphide can suppress all activity is because the actual effective atoms of catalysts are relatively few in number, and are in the most favourable position to form adsorption compounds of maximum permanence with approaching molecules of any kind, be they interactants or "poisons."

The diminution of activity of palladium and platinum in presence of small proportions of certain adsorbed metals, which was carefully studied by Maxted,[27] can be readily understood from the same standpoint.

The same explanation holds for the poisons which do not, as a rule, proceed to form definite compounds with the component atoms of the surface. Pease and Stewart,[28] for example, have shown that a copper catalyst which is capable of adsorbing 1 c.c. of hydrogen has its hydrogenating activity reduced by over 90 per cent. if 0·03 c.c. of carbon monoxide is also adsorbed, although the adsorption capacity for hydrogen is not markedly altered. The carbon monoxide, which is adsorbed in preference to hydrogen, is evidently held mainly at those atoms which are most effective in hydrogenation.

With carbon monoxide, and no doubt in similar cases where a definite stable compound is not produced, it is easy to understand that the poisoning action is rather of an "anæsthetic" than of a definitely "toxic" nature, for under suitable conditions the carbon monoxide can be displaced from the catalyst, the activity of which is then found to revert to the normal.

Although it is convenient to retain the old terminology of catalyst poisons and catalyst promoters (accelerators),

it is really obvious nowadays that the main factor which determines both effects is that of selective adsorption of one or other component present in the interacting system. Formerly, of course, these effects appeared very complex, mysterious and difficult to understand; the amount of poison or accelerator necessary to produce very marked effects being so extremely small in comparison to the weight of reacting material, or even of catalyst. The operation of selective adsorption at a surface such as that outlined on p. 21 brings into line the phenomena of inhibition or poisoning, some of the means by which the activity of a catalyst can be apparently enhanced, and also cases of what is known as "beneficial poisoning"—all of these being different aspects of one and the same fundamental condition.

"Beneficial poisoning" is the case in which a catalyst reaction is slowed down by the presence of a specific material in such a way that the catalytic process stops short at an intermediate stage in the sequence of a possible chain of reactions. For example, Sabatier and others showed that if a mixture of acetylene and hydrogen in equal volumes was passed over catalytic nickel there is invariably obtained a mixture of ethane and unchanged acetylene, no ethylene being produced; work by Ross, Culbertson and Parsons,[29] however, has indicated that if the nickel surface is first saturated with acetylene alone and then treated with a mixture of acetylene and hydrogen, ethylene can be produced in some quantity. The covering of the entire nickel surface with adsorbed acetylene in the first instance appears to restrict the adsorption of hydrogen with consequent retardation of the hydrogenating reaction.

An excellent example of the utilisation of beneficial or protective poisoning is the preparation of aldehydes from acid chlorides by the method of Rosenmund, Zetsche and Heise.[30] These authors found that if benzoyl chloride in solution in pure benzene is hydrogenated in presence of colloidal palladium only

traces of benzaldehyde are produced, whereas if ordinary benzene (containing thiophene) is used, good yields of benzaldehyde result. They extended their observations and found that substances such as quinoline, dimethylaniline or quinoline heated with sulphur all had similar good effects on the yield of aldehyde obtained in this reaction, whilst it was also found that the use of palladium on a support containing sulphur (*e.g.*, barium sulphate) assisted to the same end. The action here is to restrict hydrogenation to the comparatively simple replacement of chlorine by hydrogen, whereas in the absence of impurities in the system the resulting benzaldehyde would be further hydrogenated and/or polymerised. By employing palladium partially poisoned to varying extents, benzoyl chloride has been reduced to benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether and toluene; most other acid chlorides behave similarly.

Finally, the employment of water as a protective poison may be referred to: this probably occurs in many processes, but has been particularly pointed out in the case of oxidation or dehydrogenation of alcohol vapours at the surface of metallic copper. Both the oxidation of methyl alcohol to formaldehyde, the decomposition of ethyl alcohol into acetaldehyde and hydrogen by copper, and the hydrogenation of acetaldehyde to alcohol in presence of nickel proceed with considerably improved yields of the desired products if a suitable proportion of water vapour is present in the system at the same time; it is presumed that the metal adsorbs the water vapour to some extent preferentially to the organic compound, with the result that side reactions of the latter are minimised.

In the course of describing many of the technical processes dealt with in Section II. of this book, attention will be directed repeatedly to various phases of catalyst poisoning, all of which should be correlated by the reader with the general theory as illustrated in the foregoing paragraphs.

Catalyst Stimulants.

It has already been stated that the enhanced activity observable in some catalysts, in presence of minute amounts of added materials either in the reacting system or in the solid catalyst itself, is also probably to be explained on the basis of selective adsorption. It should be noted, however, that in the cases in which this principle is utilised in technical practice it usually takes the form of the employment of what are known as mixed catalysts, that is to say, catalysts consisting of a major component with minor amounts of the accelerating or "promoting" substance. It may sometimes happen that a component of the system exterior to the catalyst has a definite accelerating rather than a retarding effect on the particular chemical change; thus it has been stated from time to time that the presence of small quantities of oxygen in hydrogen has a beneficial action on various hydrogenation processes, either by way of general acceleration, or by minimising the production of an undesired by-product (thus the presence of about 0·2 per cent. of oxygen in the hydrogen used in the reduction of acetaldehyde in presence of nickel is said to prevent the formation of small quantities of ether in the resulting ethyl alcohol).

In the great majority of cases, however, acceleration or even apparent initiation of a definite catalytic change results from the presence of solids added to the main catalyst. The illustration of the mechanism by which these changes in behaviour are effected has not proceeded by any means so far as that of the action of poisons, but it appears most probable that the primary function of the added material ("promoter" or "stimulant") is to alter the general conditions of adsorption at the solid surface, with the result that the ensuing chemical change takes a different course. Evidently, therefore, this is a much more complicated case to investigate than that of the selective adsorption of different gaseous or liquid compounds at a relatively simple solid surface, and it is not surprising that it is

somewhat difficult at present to distinguish the wood from the trees.

A few illustrations will be given, in support of the above general statement, and in order to give some general indication of the possible mechanism of various mixed or promoted catalyst processes which will be referred to later in this book, from selected cases which have been studied from the theoretical point of view; the subject is very fully considered from a theoretical standpoint in Rideal and Taylor's "Catalysis in Theory and Practice."

One general word of warning, however, may be offered to the student of catalyst promoters, namely, that the patent literature is crowded with claims for mixed catalysts of all kinds for the carrying out of all manner of processes. Certain of these patents, probably many of them, are undoubtedly the result of sound observation and form well-authenticated instances of catalyst stimulation; but there is no doubt that in many other cases the claims have not been sufficiently well studied, or have been multiplied considerably beyond what experimental facts may justify. Consequently the abundant information in the patent literature cannot be accepted, in the case of catalyst promoters, as in any way suitable matter for the indiscriminate collection of data on which to base any explanation of the phenomenon.

(i.) *Mixed Metal Catalysts.*—These are amongst the first cases in which promoter action was definitely recognised. The Badische Anilin und Soda Fabrik,[31] in the early stages of their hydrogen and ammonia syntheses, investigated an enormous number of mixed metal catalysts for both processes and, for example, succeeded in replacing the more expensive uranium or osmium ammonia catalyst by iron, nickel or similar metal in association with a metal such as molybdenum or bismuth.

So far as laboratory actions are concerned, Ipatiew [32] had published observations prior to the

Badische work to the effect that the presence of iron favoured in some cases the activity of copper as a hydrogenating catalyst, and also that a mixed nickel-alumina catalyst could effect the combined hydrogenation and dehydration of, for example, camphor to camphene or phenol to cyclohexane at a temperature 100°–150° lower than that necessary for either hydrogenation over nickel alone or dehydration in presence of alumina alone.

Other cases of mixed metal catalysts (usually with one metal very largely preponderating) will be found in many other instances, but the information regarding them is largely empirical and does not indicate much as regards the mechanism of the promoter action.

One of the cases which has received detailed study is the reduction of copper oxide and of mixed copper-nickel oxides. Pease and Taylor [33] have examined the reduction of copper oxide at moderately low temperatures and have shown that the action proceeds practically entirely at a copper oxide-copper interface (reduction does not proceed freely until copper nuclei have been produced in the oxide mass). Armstrong and Hilditch,[34] examining the fact, recorded by Dewar and Liebmann,[35] that copper nickel catalysts could be reduced at or below about 200° with production of active catalytic nickel, showed that reduction of nickel oxide only occurred at the lower temperature (and active catalysts only resulted) when the copper and nickel had been precipitated together in the form of a double carbonate; thus the proximity of the copper and nickel oxides must be of a molecular order before reduction of the nickel takes place. These two sets of data taken in conjunction with each other offer some hints as to the interplay of one metal on the other in the catalyst surface

(ii.) *Metal-Metal Oxide Catalysts.*—The cases in which a metallic catalyst has its properties altered or stimulated by the presence of traces of irreducible oxides are very numerous and may be divided into two

classes, namely, those in which the oxides are of a neutral or feebly acidic type, and those in which they are definitely alkaline. We will consider the former class first of all.

One of the most carefully studied cases so far is the influence of small quantities of oxides such as silica, alumina, thoria, iron oxide, etc., on the activity of hydrogenating catalysts, especially nickel. It has been established that the presence of very small percentages (1–2 per cent.) of alumina or silica co-precipitated with an unsupported nickel catalyst produces the dual effect of very materially increasing its activity and also of appreciably increasing its stability, especially with regard to the effect of temperature. The apparent volume of such promoted catalysts appears to be in general greater than that of pure nickel, and the adsorption capacity of such catalysts for ethylene, hydrogen, etc., is similarly increased. Beyond this it cannot be said that there is any clear experimental evidence concerning the mechanism of the stimulation in activity.

Reference should again be made here to the case of supported catalysts ; for example, nickel mounted upon powdered pumice, fuller's earth, diatomaceous earth, powdered silica gel or charcoal, etc. With the exception of the last, all these supports consist essentially of oxides of the type that we are considering at the moment, but their influence on the catalytic activity of the nickel differs widely. For example, nickel mounted on charcoal, pumice and most types of fuller's earth is little less sensitive to temperature than unsupported nickel, and its activity is not materially enhanced (except in the case of activated charcoals of the modern type). Here it appears that there is little or no mutual influence between the ultimate particles of the support and of the nickel, the former serving merely as a mechanical basis for the nickel and aiding in mechanical properties such as ease of passage of gas, ease of filtration and so on. On the other hand the highly activated

charcoals, most kieselguhrs or diatomaceous earths, and also powdered silica gels have a very marked stabilising action on the resistance of the catalyst to higher temperatures, and also an equally marked effect on the temperature of reduction of nickel oxide deposited on these materials.

For example, a temperature of 350°–400° may be required in order to obtain efficient reduction of nickel on an active charcoal, whilst on kieselguhr at low concentrations (10–20 per cent. Ni) reduction does not set in vigorously below 420°–450°, and in similar cases with silica gel as a support a temperature of 550° or even higher may be necessary for reduction.

Again, the composition of the oxides forming a porous support of the type of kieselguhr has considerable influence on the activity of the resulting catalyst; nickel mounted on a pure silica diatom structure is usually distinctly less active than if alumina is present in or has been added to the diatomaceous material. It therefore appears that the influence of the added oxide is largely specific, although it is not known yet with any precision what occurs in the actual promoted catalyst surface. Taylor's view on the basis of his picture of the catalyst surface would appear to be that the presence of oxide molecules, adjacent to or interspersed among the nickel atoms in the outer layers of the catalyst, not only serves to diminish cohesive attraction between the metal atoms but also exerts specific selective adsorption effects, due to the adsorption capacity of the oxide " ions " in conjunction with that of the nickel atoms.

(iii.) *Metal-Alkali Catalysts.*—These form another important group of promoted catalysts, since the most common type of catalyst at present employed in ammonia synthesis consists of reduced iron coupled with an alkali such as sodium carbonate, potassium carbonate, lime, etc., in small quantities. The action of the alkaline oxide is not simple to explain, but the adsorption and other physical phenomena of an alkali-promoted iron catalyst exhibit corresponding paral-

lelisms with the increase in efficiency over the pure metal catalyst.

Another case which is more readily understandable on chemical grounds is the influence of an iron-alkali catalyst on the union of carbon monoxide and hydrogen, when the formation of condensed chain compounds containing up to eight or nine atoms of carbon is observed; the tendency to condensation can readily be understood as a result of the intervention of alkali in the chemical changes involved, on lines discussed in dealing with the "synthol" process in Section II., Chapter II (p. 93).

Finally, notice may be taken of the advantageous effect of the presence of a very small amount of sodium carbonate in the hydrogenation of liquid phenols by nickel. The maximum effect is apparently reached when the alkali concentration is about 25 per cent. of that of the free metallic nickel present, and the rate of hydrogenation becomes more nearly linear than when the alkali is absent. This implies that in some way the nickel is being kept more free from toxic action, and it may be that the acidic action of phenol on the nickel is in some way restrained by the presence of adsorbed alkali.

(iv.) *Mixed Oxide Catalysts.*—Considerable attention has been paid to the theoretical study of mixed oxide catalysts in the case of mixtures of oxides of iron, chromium and cerium, or of manganese and copper, or of manganese, copper and silver; these mixtures very readily convert carbon monoxide to dioxide in presence of atmospheric oxygen.

Another important case of mixed oxide catalysis is the production of methyl alcohol from water-gas in presence of zinc oxide. Zinc oxide alone was at first discovered to be a reasonably active catalyst for this change, but later it was found that combinations of zinc and chromium oxides were far more efficient than the former alone, and more efficient than various mixtures of zinc with other oxides; recent work by

Taylor and Kistiakowsky [36] has again demonstrated that the most efficient (zinc chromate) catalyst has by far the greatest adsorptive power of the series with respect both to carbon monoxide, hydrogen and methyl alcohol.

The connection between adsorptive capacity and the action of catalyst promoters is indeed sufficiently clear, although precise understanding of the details of the stimulatory processes involved is not yet forthcoming.

Other important cases of mixed metallic oxide catalysts are those used in certain oxidation processes, notably the German processes for the oxidation of ammonia to nitric acid, in which a mixture of iron oxide with a little oxide of a metal of variable valency (usually bismuth) forms the catalyst. The mechanism of promoter action in this case will no doubt eventually be brought into line with that of hydrogenating and other catalysts ; all that may usefully be said at the moment is that it is evident, both in this and other cases of oxidation, that the presence of an element which has the capacity of more or less readily forming a series of oxides (*e.g.*, manganese, cerium, vanadium, bismuth, etc.) is invariably connected with the stimulation of catalytic oxidation.

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CHAPTER III

THE ACTION OF ENZYMES

The study of chemical actions effected by living organisms has naturally been prosecuted most largely in connection with physiology and pathology, and has consequently developed on somewhat different lines from those on which, for example, catalysis at solid inorganic surfaces has been investigated. Nevertheless it is now agreed that chemical actions conditioned by living organisms are effected by biochemical catalysts to which the generic term enzyme has been given, and that the general principles on which the latter act are substantially the same as those which govern any other form of catalysis. Investigation of the behaviour of enzymes is, however, more complicated and difficult than that of a solid inorganic catalyst, because the enzymes are only produced by living cells, they are far more complex in composition and specific in their action than inorganic catalysts, they exist in the form of colloidal solutions and are very delicate and exceedingly sensitive to the influence of temperature or extraneous chemicals. Thus their activity is, in general, retarded even by accumulation of the products of the chemical action which they induce or accelerate.

We have merely to consider the cases in which enzyme action is, or may be, employed as a means of manufacturing chemical compounds in bulk, and to this end it is sufficient to dwell on those aspects which determine the general conditions under which successful technical operation of enzyme actions is most likely to be realised. The vast literature on the function of fermentation processes of all kinds in the animal or plant organism does not concern us except in so far as it assists in the exploitation of specific ferments or

enzymes in the factory ; those who are interested in more general aspects of enzyme action will turn to treatises such as " The Nature of Enzyme Action " (Bayliss), or other appropriate monographs.

The nomenclature used by biochemists differs to some extent from that familiar to the ordinary technician, and a few definitions may be inserted at this point.

The term *ferment* was formerly applied generally to living organisms (such as yeast, fungi, bacteria or specific parts of more complex living bodies) which possessed the power of effecting chemical change in a compound (such as starch, sugar or protein) ; when it became recognised that the active chemical agent was not the living cell or organism itself, but a component of the latter, usually soluble in water, and certainly separable from the living matter, the active agent was referred to as a soluble or " unorganised " ferment, or, in modern phraseology (Köhne[1]), as an *enzyme*. An *enzyme* is therefore a biochemical catalyst (Effront[2]), and consists of a very complex colloidal organic molecule, which is not living (protoplasmic), but which is only producible at present by a living organism.

Enzymes are classified largely according to the type of compound upon which they exert chemical action. Broadly speaking, we are dealing with a catalytic system in which the catalyst is an *enzyme :* the substance acted upon is often referred to as the *substrate*, although other terms are used. For example, in actions of hydrolysis (*e.g.*, cane sugar to invert sugar), the compound hydrolysed is called the *hydrolyte*. The general action of an enzyme is often referred to by adding the suffix *-lytic* to the generic name of the substrate ; etymologically it is preferable to use the suffix *-clastic* (H. E. Armstrong[3]). Thus a starch-fermenting enzyme is *amyloclastic*, one which decomposes protein is a *proteoclastic* enzyme, etc.

The individual names of enzymes are partly fortuitous, partly rational. The older, better-known, bodies

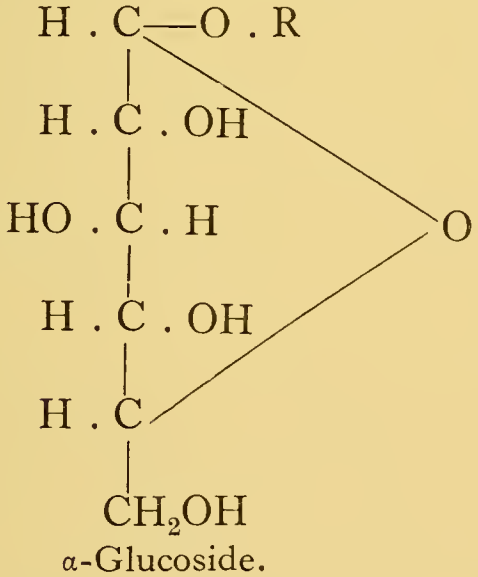
received specific names, such as diastase, pepsin, trypsin, emulsin, etc., which have become more or less fixed by long association ; incidentally, some of these probably consist of mixtures of enzymes. Latterly it has become usual to follow the suggestion of Duclaux, namely, to denote a specific enzyme by adding the termination *-ase* to that of the particular substrate acted upon ; thus lactase is the enzyme which hydrolyses lactose, urease that which decomposes urea, and so on.

It has already been said that enzymes are colloidal in nature : in consequence a solution of an enzyme in water consists of a dispersion of the colloidal particles throughout the liquid phase, and behaves as a heterogeneous, rather than a homogeneous, system. It will be shown below that the study of enzyme action has proved to be that of an operation which is taking place at a surface, namely, the interface between the colloidal enzyme and the substrate solution. Thus, from the point of view of catalysis, the process falls into line with the heterogeneous actions discussed in the preceding chapter.

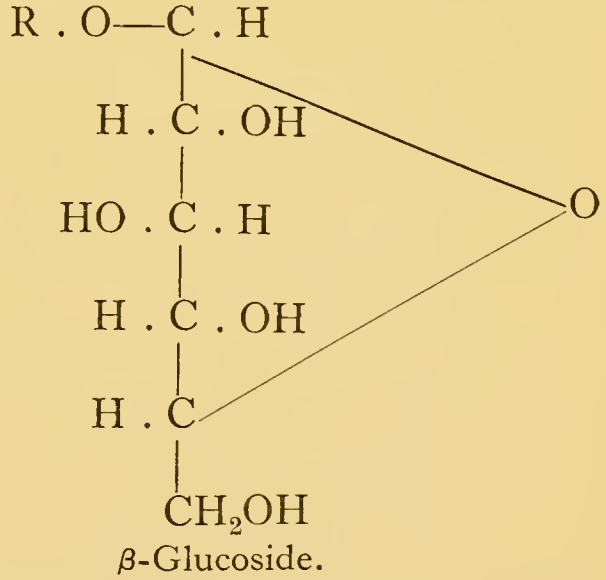
The colloidal, complex nature of the enzymes has made it, however, hitherto impossible to isolate any one of them in a pure condition. Other colloidal compounds are invariably present along with enzymes in the cell, and the product usually obtained is a preparation of which the active enzyme forms only a (frequently subsidiary) proportion. " Crystalloid " compounds which are also present in the cell-juices can be removed to a large extent by dialysis, and advantage can sometimes be taken of the differing electrical charges of the colloidal components of the mixture to effect some separation by selective adsorption on an electro-positive (*e.g.*, aluminium hydroxide), or an electro-negative (*e.g.*, kaolin) inorganic material. By combination of such methods Willstätter[4] and co-workers have prepared relatively concentrated specimens of amylase, invertase, lipase, peroxidase and trypsin, the activity

of which was found to be many hundreds of times that of the starting-out material. Even in the most highly-active products, however, it has hitherto proved impossible to assign any definite chemical composition to an enzyme, and it is doubtful if a close approach to the isolation of a pure enzyme has yet been effected. Consequently it would appear that the activity of an enzyme *per se* is extraordinarily high, and may, if it is possible to make the comparison, be intrinsically greater than that of an inorganic catalyst surface.

However this may be, it is certain that the specificity of action of enzymes far surpasses that of the ordinary inorganic catalyst ; in general, the action of an enzyme is restricted to a few closely-allied kinds of—or even to one single—substrate. Of many possible instances, the familiar one of the hydrolysis of the stereo-isomeric α- and β-glucosides is probably still as striking as any ; the only difference between these lies in the configuration of the hydroxyl group which is concerned in the formation of the glucoside, yet whilst α-glucosides are hydrolysed by maltase but not by emulsin, the reverse holds for β-glucosides, which are readily attacked by emulsin but not by maltase :—



α-Glucoside.



β-Glucoside.

It is a frequent occurrence in metabolic changes that a specific transformation of a given compound is effected by a definite enzyme, which is produced at the seat of action and may only be effective for the parti-

cular change in question. In other cases, especially where the chemical change concerned is a relatively simple one, such as hydrolysis, the same enzyme may be capable of acting upon a number of compounds, so long as the configuration of the molecule is compatible with the enzyme. Thus emulsin will hydrolyse the synthetic β-methyl-glucoside, nearly all of the many natural β-glucosides (such as amygdalin, salicin, quercetin, etc., etc.), tetramethyl β-methylglucoside and even β-methyl-*d*-isorhamnoside (derived from the methyl-pentose *d*-isorhamnose, containing a chain of six carbon atoms and the same configuration as *d*-glucose); but it is without action on β-galactosides (differing from *d*-glucose in configuration) or on β-methyl-*d*-xyloside (*d*-xylose has a similar configuration to *d*-glucose, but is a pentose with a 5 carbon-atom chain). In a few instances an enzyme is more generally active; lipase, the enzyme present in castor oil and other seeds, for example, exerts hydrolysing powers on a comparatively wide variety of compounds belonging to the class of fats and other esters of the fatty acids.

It should be added that enzyme action is held to be generally reversible; for example, an enzyme which hydrolyses a compound is able, under suitable conditions, to build it up. This was shown for the maltose-glucose change by Croft Hill,[5] for the action of lipase by H. E. Armstrong and Gosney[6] and for glucoside hydrolysis and synthesis by the researches of Bourquelot and Bridel;[7] and has also been established in a number of other instances.

It should be noted that in most instances the products spoken of as individuals, *e.g.*, maltase or emulsin, are probably mixtures of two or more enzymes, each of which may have specific properties.

E. F. Armstrong compares the relation of enzyme to substrate with that of a glove fitted on a right hand: if the position of any finger be altered it is impossible to fit the glove; further, the glove will not fit on the left hand. Emil Fischer originally compared the relation-

ship to that existing between a key and the lock for which it is made.

It is widely held at the present time that the ultimate enzyme molecule may be a complex, perhaps labile, colloidal system of high molecular weight, a (perhaps relatively small) part of which may consist of groups of atoms or radicles, whose configuration enables them to fit that of a specific substrate and whose chemical constitution is probably frequently related to that of the latter. On this hypothesis the reactive part of the enzyme molecule might well be compared with a heterogeneous catalyst combined with a more or less inert support (*cf.* pp. 25, 35).

This leads us to the more general question of the kinetics and mechanism of enzyme action, the study of which has led biochemists to very similar conclusions to those reached by the workers in the field of contact actions at solid surfaces.

Measurement of the rate of chemical change effected by enzymes, in the hands of many workers, has given results of a complicated character. In many cases a considerable part of the change has appeared to follow a unimolecular or logarithmic course with respect to the disappearance of the substrate, but not infrequently the rate of action was observed to fall below that required for a unimolecular change as the fermentation progressed. Contrariwise, instances have been observed (*e.g.*, the work of Victor Henri[8] with invertase and cane-sugar) in which the rate was consistently greater than that of a unimolecular action. Such observations are now known to have been due to the operation of various conflicting factors, the nature of which will be explained a little later.

E. F. Armstrong,[9] in the case of hydrolysis of cane-sugar by enzymes (and also by acids), definitely showed, in a series of communications in 1904, that the shape of the hydrolysis-time curve was ideally linear, and that this was to be expected on the hypothesis of a combination between enzyme and substrate, whilst the relation-

ship between the rate of reaction curve and the proportions of enzyme and substrate were likewise explicable on this basis. Similarly, in 1906, Bayliss[10] suggested that the rate of change in enzyme action is a function of the degree of adsorption of the substrate by the enzyme at different stages of the reaction.

The work of H. E. and E. F. Armstrong, Horton and others[11] in 1913 on the action of urease on urea

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$

confirmed the fact that, if the products of the action were removed from the system and no conditions obtained which affected the activity of the enzyme preparation, the amount of decomposition per unit of time approximated to a constant figure throughout the whole of the reaction.

In other words, just as in the hydrogenating action of nickel studied at a later date (*cf.* p. 17), the essential rate of enzymic change is " nul-molecular," a constant amount of substrate being acted upon throughout in equal intervals of time. This has led H. E. Armstrong to express the opinion that " enzymic action takes place entirely at the surfaces of colloid particles suspended in the solution of the hydrolyte and not between substances which are all in true solution."

In the last (1925) edition of his " Nature of Enzyme Action," Bayliss sums up the mode of enzyme action as the sequence of (*a*) *diffusion* of the enzyme through the substrate solution (a relatively minor part), (*b*) *adsorption* of the interacting substances on the surface of the enzyme particles (practically instantaneous), and finally (*c*) actual chemical interaction between the substances brought together on the surface (usually the slowest of the processes concerned, and therefore that controlling the rate of action as a whole). It is unnecessary to stress the close correspondence between these views and those which have been arrived at on independent grounds in the case of the contact actions dealt with in the preceding chapter. It should also be pointed out that " adsorption " of substrate by

enzyme is apparently regarded by the majority of biochemists as a very pronounced combination between these bodies as the result of selective affinity, and that it has been emphasised, especially by the school of Professor H. E. Armstrong, that combination of the enzyme with both the substrate and the other party to the chemical change (*e.g.*, both hydrolyte and water), precedes the actual chemical transformation.

This tendency to combination with the enzyme (adsorption) is also shown to a marked degree by most of the products of enzyme action, and in appropriate circumstances the enzyme may be more or less put out of action owing to its adsorption of the products. Hence, as the latter accumulate, the effective concentration of the active enzyme falls off, leading to rate of action curves which frequently approximate to the logarithmic type. This was especially well illustrated in the course of the studies of urease previously mentioned.

Again, increase in the concentration of the substrate beyond a certain point tends towards saturation of the enzyme surface by the latter, with consequent retardation of chemical change ; consequently it is usual to find that enzyme action proceeds most readily when the substrate is in a state of considerable dilution—a point of some technical importance.

Other factors which influence the activity of enzymes include the acidity or hydrogen ion concentration of the solution and the amount of electrolytes present. Most enzymes are very sensitive to slight changes in the acidity or alkalinity of the solution, and are most active only at a definite point ; the exact " hydrogen ion concentration " which is most effective varies according to the enzyme, the usual range being from media slightly more acid to media slightly more alkaline than pure water. (The hydrogen ion concentration of conductivity water is $\frac{1}{10^{7\cdot07}}$, or $10^{-7\cdot07}$; employing the conventional expression introduced by Sören-

sen,[12] we say that water has the p_H value of 7·07, more acidic solutions having lower, and more alkaline solutions higher, values of p_H.)

The presence of electrolytes in solution usually has an appreciable effect on the general rate of action. This is doubtless related to their colloidal nature, in consequence of which the effective surface of the particles may be expanded or contracted according to the concentration of electrolyte in the system.

The above factors are not definitely operative in the case of most solid or non-organised catalysts (of the types dealt with in the preceding chapter), but we come, in conclusion, to other causes of alteration in enzyme activity which are closely parallel with those affecting the ordinary contact agent in heterogeneous systems, namely, temperature, stimulants and toxic agents (or, as the latter are termed in biochemistry, co-enzymes and anti-enzymes).

Enzymes are active only over a comparatively narrow range of temperature and exhibit maximum sustained activity at an optimum temperature characteristic for each enzyme. Enzyme action is practically negligible at 0°, but with rise of temperature the activity is increased from twofold to sevenfold for each increment of 10°. For most enzymes the optimum region of temperature lies at a point between about 25° and 38°; certain bacteria which decompose some forms of cellulose are most active at 68°–70°, but this is quite exceptional. The *initial* activity of an enzyme continues to increase beyond the optimum temperature, but its *sustained* activity declines rapidly and, at a certain point (usually between 70° and 100°), all activity ceases. Enzymes are destroyed by exposure to a temperature of the order mentioned, and it is believed that this is the result of a "coagulation" effect whereby the colloidal surface is destroyed. These phenomena were formerly held to differentiate enzymes from inorganic catalysts, although Ernst[13] showed that colloidal platinum sols exhibited exactly the same series of

phenomena; as a matter of fact, however, very similar relationships between activity and temperature are observable in the case of solid contact agents (*cf.* p. 26), the only differences being the generally wider range of temperature over which activity is exhibited and the fact that these temperatures are of the order of, say, 200°–500° instead of 0°–100°.

The question of inorganic catalyst stimulants or "promoters" has been discussed in Chapter II (pp. 32-38). Parallel with this we have the influence of "co-enzymes" on enzyme action. In several instances it has been found that a substance (frequently crystallised and removable by dialysis) is always produced along with the enzyme, and that in its absence no activity is exhibited. Thus Harden and Young [14] found that the enzymes of yeast-juice, after separation from the aqueous medium by expression on a gelatin filter, had no power to ferment sugar solutions; nor, of course, had the aqueous filtrate; but the fermentation proceeded normally when filtrate and colloid residue were again mixed. Similarly, liver lipase or pancreatic juice lose their specific activities after dialysis, but activity is resumed on adding to the colloid the dialysed liquid, or even, in some cases, solutions of specific salts. The mechanism of action of co-enzymes is little understood at present. Whilst the presence of a suitable electrolyte in appropriate concentration (*e.g.*, sodium chloride, potassium nitrate, or sodium phosphate) seems the main factor in some cases, in others this is not sufficient; thus filtered yeast-juice (zymase) is not restored to activity by the simple presence of a phosphate solution, although phosphates are necessary. There is reason to believe that the actual "co-enzyme" in this case is a hexose-phosphoric-acid ester.

Finally, enzyme action is retarded by many substances which are of the nature of "catalyst poisons" or "anti-enzymes." On the one hand there is some evidence that enzymes in a living body tend to the production of "anti-gens," *i.e.*, bodies which oppose

their action ; on the other there are abundant examples of the retarding effect of different chemical compounds on enzyme activity. Thus many proteins will retard the specific action of enzymes, such as emulsin or lipase, whilst these are equally or more susceptible to many simpler compounds such as, for example, hydrocyanic acid. It may well be surmised that these effects are conditioned by one or other of the following causes ; selective adsorption or excessive general adsorption of the anti-enzyme at the active surface, changes in the colloidal state and surface of the enzyme induced by the presence of the anti-compound in the substrate solution.

Turning to the bearing of these observations on the practical applications of fermentation, it will be realised that the problems encountered will in many ways be similar to those concerning inorganic catalysts, but the active agents are still more delicate and work within a more restricted range of temperature ; beyond this, however, are the specific problems connected with the production and maintenance of an agent produced only from a living organism. In practice, up to the present, the use of enzymes apart from their living progenitors is the exception rather than the rule, and it is the more general practice to employ cultures of specific organisms or microflora which develop enzymes of appropriate properties. The most familiar example is the yeast plant, *Saccharomycetes* sp., whilst the use of fungi, such as *Mycoderma*, or of bacteria, such as *Bacillus butyricus*, may be cited as typical instances of other classes of organisms. The technical production of enzymes is thus a bacteriological problem ; it involves the selection of a medium in which the enzyme-content is maintained or replenished by adequate growth of the organism, and the exercise of precautions against infection of the medium by unwanted organisms different from the desired species.

Usually, therefore, in addition to the substrate it is necessary to provide specific nitrogenous material,

inorganic salts, etc., in order to facilitate the growth of the enzyme-producing organism, whilst, as well as providing the necessary nutrients in this way, it is essential to carry out the fermentation process under rigorously sterile conditions. Furthermore, the various factors discussed above with reference to the presence of accelerating and retarding materials must be borne in mind.

Finally, the economic advantage of an enzyme process is, as has already been emphasised, largely bound up with the relatively low operating temperature, a temperature which, however, must be fairly closely controlled ; whilst a possible disadvantage, in many cases, resides in the dilute solution of substrate, which is often necessary for vigorous fermentation, a factor which not infrequently leads to a still more dilute solution of the ultimate technical products. In spite of these seeming difficulties there is undoubtedly scope for far more extended scientific application of these natural catalysts than has hitherto been made.

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CHAPTER IV

THEORETICAL ASPECTS OF CATALYSIS IN HOMOGENEOUS SYSTEMS

QUANTITATIVE investigations connected with the theory of catalysis in homogeneous systems may be said to commence with Wilhelmy's famous study[1] of the rate of inversion (hydrolysis to glucose and fructose) of cane-sugar solutions in presence of mineral acids. He showed that the amount of sugar inverted at any moment was proportional to the quantity of sugar present at that time, and also that the rate varied according to the concentration of the acid and the temperature of the system. In the hands of Ostwald, Arrhenius and others the mathematical treatment of reaction velocity as conditioned primarily by the law of mass action was systematically developed, but the first example of a unimolecular action to be definitely analysed is to be found in Wilhelmy's work. In 1862 Löwenthal and Lennsen[2] made an important extension to this investigation by showing that the rate at which acids invert cane-sugar is proportional to the strength of the acids, and Arrhenius,[3] in connection with his electrolytic dissociation theory, showed that in sufficiently dilute solutions the rates of hydrolysis of cane-sugar or of simple esters conditioned by various mineral acids were exactly proportional to their degree of electrolytic dissociation into ions.

It thus became clear that the catalytic action of acids in hydrolysis was closely connected with the number of hydrogen ions present, the stronger, more completely ionised acids possessing high catalytic activity. Similarly, the work of Reicher[4] and others showed that the rate of hydrolysis conditioned by dilute alkali solutions was explicable as an action catalysed by hydroxyl ions.

The converse process of esterification was first studied from a similar point of view by Berthelot and St. Gilles[5] for a number of cases of simple, non-catalysed reactions of the type

$$\text{alcohol} + \text{acid} \rightleftharpoons \text{ester} + \text{water}.$$

The use of sulphuric acid as an esterifying agent had been practised for a long time prior to the realisation that its action was catalytic, and that, as shown by Victor Meyer and Sudborough,[6] and by E. Fischer and Speier,[7] it could be replaced with advantage in many organic preparations by the stronger and more active dry hydrochloric acid, employed in small proportions (*e.g.*, from 1–3 per cent. of the mixture of alcohol and acid). Senderens[8] and his colleagues demonstrated much later that not only sulphuric acid, but also anhydrous aluminium sulphate or potassium hydrogen sulphate, are also efficient esterification catalysts when present in quite small concentrations.

The above classical researches have led to an immense volume of experimental work by many well-known investigators on various problems related to catalytic esterification, dehydration, and hydrolysis in homogeneous systems, such as the constitutive influences exerted by one or both of the interacting organic molecules, the anomalous behaviour of strong acids and bases in other than small concentrations, and many similar factors. Other types of homogeneous catalytic action have received less frequent study from the kinetic standpoint, but reference may be made to Steele's examination[9] of the Friedel Crafts condensation from this point of view; Steele was led to the conclusion that the action depended on the formation of unstable intermediate-complexes of the catalyst (aluminium or ferric chloride) with each interactant (aromatic hydrocarbon and organic halogen compound) and also with the organic product of the action.

In the case of processes involving the addition or elimination of water, it has been increasingly apparent that the simple ascription of catalytic power to hydrogen

or hydroxyl ions is insufficient to explain the observed facts, since it can only be quantitatively correlated with the latter in particular cases (namely, actions proceeding at great dilution with respect to the acid or base present).

Concurrently with the development of the Arrhenius theory there has been a considerable amount of work carried out by H. E. Armstrong[10] and his students on the processes operative in solution, their fundamental hypothesis being that hydrolytic action results from an interaction between the hydrated compound, which is being decomposed, with the hydrated catalyst. Armstrong regards all chemical action as "reversed electrolysis" and maintains that a three-component circuit comprising the two interactants with a catalyst is in all cases essential to chemical action.

Simple kinetic studies of the rate of homogeneous catalytic actions, whilst useful in clearing the ground and indicating the general conditions operating, are not by any means entirely adequate to solving the problem of how the catalyst comes into play. The latter question is, indeed, more elusive in the case of homogeneous than of heterogeneous actions, because in the latter case it is possible not infrequently to choose conditions of observation which permit evidence to be gained as to what is going on at the catalyst surface itself, as distinct from the average behaviour of the whole of a homogeneous medium. Consequently the study of the function of a catalyst in a homogeneous system is much more difficult than in the other case, and it cannot be said that the explanations available up to the present are as explicit and generalised as in the case of contact actions (incomplete as the latter admittedly are).

Investigation of the subject, moreover, is being conducted on lines which, for the most part, are somewhat remote from industrial applications, and reference should be made, for example, to Rideal and Taylor's "Catalysis in Theory and Practice" and to the Reports of the American Committee on Contact Cata-

lysis (1921–1927) for a more adequate description of recent work on the theoretical side of this question. The brief *résumé* given below will indicate that attention is being increasingly directed to the question of how the interacting molecules in a homogeneous system are " activated " by the intervention of a catalyst, *i.e.*, the manner in which energy is conveyed to the interactants. This fundamental aspect of catalysis goes, perhaps, more deeply into the matter than is necessary for the normal efficient application of catalysis in industry. Obviously, it is a most important —from a purely academic standpoint it is *the* most important—side of fundamental research into catalytic action, for it will ultimately tell us *why* catalysts display their specific activity. On the other hand, it would be ample aid for the moment if the technologist had at hand the fundamental data as to *how* catalytic action is effected in all cases; and it may be recalled that the late Sir William Ramsay used to impress upon his students that, when *why* was too difficult a problem to solve, *how* was frequently more tractable and quite helpful.

Only a very short sketch of recent academic investigations into homogeneous catalysis will therefore be added here.

Reverting again to the catalytic effects exerted by acids during esterification and hydrolysis, we find that Senter[11] observed that the effect of neutral salts on the activity of the acid catalyst, and also the general temperature coefficient relationships of the process, were not directly in accord with a simple hydration of the acid or the hydrolyte ; on the other hand, his work and that of Lapworth[12] and others pointed to a specific action of water in the catalysis, and further, to the probability that the undissociated molecule of the catalytic acid also exerts a definite catalytic action in addition to, but in a certain relation to, that of the catalytic ion.

Lapworth's investigations dealt mainly with the accelerating effect of hydrogen chloride in ester forma-

tion ; the results of a large number of measurements led him to the view that free hydrogen ions are the essential catalysts, and that the presence of water is anti-catalytic owing to the free ions being rendered inert by conversion into hydrated ions. The " availability " of an acid in catalytic esterification was thus considered as a factor which depends on the relative amount of complex ions formed by association of the hydrogen ions with compounds of a " basic " type—alcohols may be regarded as exceedingly weakly basic, whilst by comparison water is definitely more basic.

These conclusions may be considered jointly with the concurrent work of Goldschmidt[13] and collaborators on the same problem, from which the latter deduced that the " active catalyst " is a compound of the interacting alcohol with a free hydrogen ion, and not the latter itself ; with Lapworth, Goldschmidt regards the retarding influence of water as due to displacement of the alcohol-ion complexes owing to the formation of hydrated ions.

Passing over many investigations conducted on similar quantitative lines and thus amenable to detailed mathematical analysis by these and other workers, reference must be made to the work of Stieglitz[14] and his students upon the interaction of imino-esters with water, ammonia or amines as influenced by the catalytic action of acids :—

$$R.C(:NH).OR' + H_2O \longrightarrow NH_3 + R.CO.OR'$$

and

$$R.C(:NH).OR' + NH_3 \longrightarrow R.C(:NH).NH_2 + R'.OH.$$

This change is very sensitive to, and markedly accelerated by, the presence of traces of strong acids, such as hydrogen chloride, and Stieglitz ascribed the catalysis to the formation of an ionised complex of the ester with free hydrogen ion ; thus :—

$$R.C(:NH).OR' + H^+ \longrightarrow (I)\ R.C(:NH_2^+).OR'$$

$$+ H_2O \longrightarrow (II)\ R.C\begin{matrix}\diagup NH_3^+ \\ \text{O} \ldots \text{H} \\ \diagdown OR'\end{matrix} \longrightarrow R.CO.OR' + NH_4^+$$

In other words the catalytic action is due to the alteration of the positive ion of a very weak base (I) into that of a stronger base (II); this theory is strongly supported by its ability to explain apparently conflicting cases. Thus, urea esters are quite stable in acid solution, whilst acylated urea esters are readily hydrolysed :—

$$NH_2.C(:NH).OR' + H_2O \longrightarrow NH_2.CO.OR' + NH_3$$
(with difficulty).

$$R.CO.NH.C(:NH).OR' + H_2O \longrightarrow R.CO.NH.CO.OR' + NH_3$$ (readily).

In the case of simple urea esters the positive ion :—

$$NH_2.C(:\ NH_2^+).OR'$$

is derived from a stronger base than ammonia, whereas the acylated urea esters are, like the simple imino-esters, weaker bases than ammonia.

On the other hand, acids readily accelerate the action of ammonia or amines upon simple urea esters, and, significantly, the product (a guanidine derivative) is a stronger base than the original urea compound :—

$$NH_2.C(:NH)\ .\ OR' \longrightarrow NH_2(C:NH_2^+)OR' + NH_3 \longrightarrow NH_2.C(:NH).NH_2 + R'.OH.$$

$$NH_2\ .\ C(:NH).OR' \longrightarrow NH_2(C:NH_2^+)OR' + R\ .\ NH_2 \longrightarrow NH_2.C(:\ NH).NHR + R'.OH.$$

Rideal and Taylor (1926, p. 341) extend Stieglitz's explanation of the catalytic decomposition of imino-compounds to the more general case of ester hydrolysis and esterification, on the principle that the essential action is the conversion (by a hydrogen ion) of a weaker base into a stronger one and that in the case of esters we have to deal with oxonium bases :—

$$R.CO.OR' \longrightarrow R.(C:OH^+).OR' + H_2O \longrightarrow R.COOH + (R'OH.H^+).$$

the alcoholic oxonium compound being more basic than the ester oxonium derivative.

All this work is exceedingly suggestive and it will be noticed that, in spite of the somewhat intangible nature of the actual catalytic agent in these cases, the trend of the conclusions is definitely away from the

older, cruder view that a free hydrogen ion or hydroxyl ion is the sole explanation of catalytic hydrolysis or esterification, and in favour of (*a*) an association or " intermediate complex " between the catalyst ion and one or more of the interactants and (*b*) of an electrochemical mechanism of the changes induced. To this extent it may be claimed as a partial experimental verification of Armstrong's original generalisation, perhaps somewhat sweeping, in 1885, that chemical action is " reversed electrolysis."

The electrochemical, or electrical, aspect of these changes has received much further emphasis from the investigations of Lapworth, Lowry[15] and others on the question of polarity—the effect on reactivity of a particular group of atoms due to its changed electrical charge, owing to the introduction, elsewhere in the molecule, of a polar atom or radicle. This affords a basis for various tentative mechanisms to account for the observed facts in different cases of esterification and hydrolysis.

Parenthetically, the reader may be reminded at this point that the more drastic processes of catalytic dehydration, whereby an alcohol is converted into ether or olefine by means of a mineral acid, have been recognised since the time of Williamson as conditioned by the intermediate formation of definite chemical compounds with the catalyst :—

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5.HSO_4 + H_2O$$

$$\begin{cases} C_2H_5.HSO_4 + C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2SO_4 \\ C_2H_5.HSO_4 \longrightarrow C_2H_4 + H_2SO_4 \end{cases}$$

Leaving the more definitely experimental or kinetic investigations, of which an outline has now been given, some reference may be made in concluding this chapter to recent study of homogeneous catalysis from the standpoint of thermodynamics.

W. C. M. Lewis[16] and others have suggested that thermodynamic or " active " concentrations of the compounds taking part in a reaction should be employed in place of the total concentrations (as used

by the older physical chemists) and on this basis Brönsted[17] has deduced that in general any bimolecular action must proceed by the formation of an unstable intermediate complex which then undergoes rapid decomposition :—

$$A + B \longrightarrow (AB) \longrightarrow C.$$

The general opinion of workers on homogeneous catalysis, in fact, appears at present to favour the view that in all cases some sort of complex-formation between catalyst and interactants takes place ; but it must be observed that the precise kind of " intermediate complex " supposed to be present by different workers on different actions takes several forms and is in most cases less defined in nature, and also less definitely substantiated at present by experimental observation, than even the adsorption phenomena established by investigators on catalysis at a solid surface. It may be said, however, that the existence of complexes during aqueous hydrolysis of esters and carbohydrates in presence of acids appears to have been definitely proved by the physico-chemical researches of Kendall.[18]

Finally, the reader is recommended to consult a recent book by Hinshelwood,[19] " The Kinetics of Chemical Change in Gaseous Systems," with reference to the question of the energy changes connected with the power of a catalyst to effect a chemical reaction. This aspect of the question was considered from a general point of view many years ago by Arrhenius, who postulated that molecules do not normally possess sufficient energy to enable them to react, but that, in order to enter into a chemical reaction, a molecule must be " activated," *i.e.*, receive sufficient additional energy to convert it into the reactive state. This energy, measured in terms of heat-energy, is known as the heat of activation (A) and may be determined in particular cases from observations of the temperature coefficient of the reaction. Hinshelwood and

Hughes [20] find that the value of A is constant when taken as the excess energy the active molecules must have, over the average energy of all the molecules, in order for reaction to occur, and that, in the case of three decompositions (those of nitrous oxide, chlorine monoxide, and hydrogen iodide), closely concordant values of A are obtained from temperature coefficient measurements and by calculation on the hypothesis of molecular collisions preceding reaction. Further, the absolute temperatures at which each of these actions proceed at the same rate are in direct proportion to the heats of activation obtained, a result which, in Hinshelwood's opinion, is the strongest and principal evidence for the reality of the "energy of activation" A.

Catalysis might therefore be regarded merely as the supply of sufficient energy to produce activated molecules, although this does not by any means explain where or how the catalyst acquires the necessary energy for transference to the interacting molecules. It is, however, generally admitted that a catalyst, from the fundamental standpoint, must have other functions than simple activation, since reaction-velocity appears to be controlled, not only by the rate of supply of energy of activation, but also by another factor or factors corresponding to the probability of reaction after activation.

The latter factor might consist merely of the probability of molecular impact by collision, or of a suitable orientation of the reacting molecules or some specifically suitable internal phase relationship of the molecule. In the latter connection attention is obviously directed to the electronic configuration or polarity of the molecule: Hinshelwood points out that if a molecule A — B receives an impact at B which directs it away from A, the small inertia of A enables it to follow B with little strain, unless A were firmly held at a surface, when A and B might be forced into a state of strain resulting in disruption. The same reasoning would

conceivably apply in a case in which A was not held at a surface, but had become attached to an electrically-charged particle, with resulting change in the electrostatic conditions existing between the intramolecular groups A and B.

Such molecular distortion can be postulated, indeed, either on electrical or other grounds ; and in the case of adsorption in a heterogeneous system the results of Palmer and Constable,[21] and of Burk,[22] suggest to the latter worker that adsorption forces can only detach atoms from molecular union if the molecule is adsorbed at more than one point by more than one atom of catalyst. This view, of " multiple adsorption," is not opposed to the more general theory of heterogeneous actions as presented in Chapter II and might, indeed, ultimately afford a more lucid explanation of such phenomena as selective hydrogenation and the highly selective action of enzymes.

It will be gathered from the present chapter that much theoretical knowledge still remains to be gleaned with reference to catalysis in homogeneous systems; but it is hoped that the outline which space has permitted will afford a general survey of the field to the reader, who is presumed to be mainly interested in catalysis for its more practical applications in industrial processes.

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SECTION II

CATALYSIS AT SURFACE OF SOLID INORGANIC MATERIALS

CHAPTER I

A GENERAL REVIEW OF TECHNICAL HETEROGENEOUS CATALYTIC ACTIONS AND THE VARIOUS FORMS IN WHICH CATALYST MATERIALS ARE USED IN INDUSTRY

So far as extent of output and importance of the products are concerned, industrial processes in which gases or liquids, or gas and liquid, are made to interact at the surface of a solid contact agent form by far the most numerous and important group of catalytic methods in technical use at the present time. This will be realised if one reflects that in this way, for example, hydrogen is produced on a scale of many million cubic feet per day—sufficient to supply light and heat to many large cities; ammonia is manufactured from nitrogen and hydrogen in various parts of the world to an extent which is already in the region of 500,000 tons of fixed nitrogen yearly; nitric acid is made from ammonia with a smaller, but still relatively large, production; sulphuric acid output in Britain is normally of the order of at least 1,000,000 tons annually, most of which is produced by the chamber process with gaseous oxides of nitrogen as catalyst, whilst the contact processes, using platinum or iron oxide as contact agent, supply the balance; and, until comparatively recently, chlorine was manufactured by contact processes to the extent of about 50,000 tons each year in this country alone.

The treatment of gases by catalytic agents does not end here; the purification of coal-gas from sul-

phuretted hydrogen and other sulphur compounds is carried out almost entirely by processes which are fundamentally contact actions at solid surfaces. In addition to this relatively long-established process, we have in quite another direction the new method of union of carbon monoxide and hydrogen to produce methyl alcohol, or (by using a different type of contact agent) a new type of synthetic fuel, if economic factors lend themselves to the use of the latter. Again, formaldehyde, the important antiseptic and organic "intermediate," has long been made technically by the combination of methyl alcohol vapour and oxygen at the surface of heated copper, whilst recent work is opening up a wide field in the controlled oxidation of many organic compounds in the vapour state by means of air in contact with certain oxides, usually those of vanadium or molybdenum. The annual output of these and some other organic compounds, produced in this way by interaction of gases or vapours in presence of appropriate solid catalysts, is, of course, much smaller in the aggregate than those of the fundamental "heavy chemicals" first referred to, but nevertheless represents an important and increasing proportion of manufactured organic chemicals.

Turning to the other aspect of heterogeneous catalysis, in which chemical action occurs in the liquid phase in presence of a solid catalyst, the most important technical application is in the case of hydrogenation processes, where hydrogen is made to unite with unsaturated liquid organic compounds of various types by the action of such metals as nickel or palladium, usually the former. The chief application of this method is the hardening or partial saturation with hydrogen of liquid fatty oils; fat-hydrogenation installations at present erected are probably capable of dealing with an annual world production of at least 500,000 to 600,000 tons of hydrogenated fats. Another important aspect of this method is the conversion of naphthalene, phenols or cresols into hydroaromatic

liquid compounds of value in the paint and soap industries, and as solvents ; whilst hydrogenation in the liquid state is also employed in the production of certain fine chemicals, perfumes, etc., such as menthol and isopropyl alcohol. Although not usually taken into account from this general point of view it should also be borne in mind that many organic synthetic processes, in which copper or other metal is a catalyst causing condensation of two molecules by removal of hydrogen chloride or other compound, are essentially instances of the technical use of heterogeneous catalysis of liquids by a solid contact agent.

The industrial methods which are to be dealt with in this section are consequently characterised by heterogeneity, not only from the standpoint of physical state, but also in regard to the widely varied kinds of materials manufactured and to the differences in working conditions and other factors which will be encountered. As already indicated, the plan adopted is primarily to group the processes according to the physical states present, commencing with gaseous actions at solid surfaces and proceeding to those cases in which the process is carried out in the liquid state in presence of a solid catalyst, one of the interactants usually, however, being a gas. This system lends itself to the separate treatment, in the first place, of water-gas catalyses (production of hydrogen, methyl alcohol, etc.), followed by that of ammonia, nitric acid, sulphuric acid and chlorine.

In order to render the subject of sulphuric acid manufacture more compact, an account of the chamber process (in which a gaseous catalyst is used and where the acting system is practically homogeneous) is interpolated after dealing with the contact process. The sulphuric-acid chamber process in its original form is one of the rare cases of a homogeneous catalytic action in the vapour phase, and, if the system of treatment were carried to a logical extreme, should be placed in a separate section following the subject of homogeneous catalysis in liquid systems.

There follow two chapters dealing with other gaseous processes effected at the surfaces either of metals or metallic oxides; the industrial applications embraced in this group are diversified, but it may be remarked that, so far as the manufacture of organic derivatives goes, the processes which have been developed are for the most part based upon the original academic investigations of Sabatier and his co-workers.

The various technical processes of catalytic treatment of liquid organic compounds in presence of reduced metals remain to be considered, and the section is concluded with a short chapter on the use of activated carbon *per se* as a catalyst in various gaseous reactions, a subject which is being developed in various quarters at present.

The general principles governing catalytic action in a heterogeneous system, so far as they are at present understood, have received attention in Section I., Chapter II, and it will be remembered that these may be summarised as follows :—

1. The possibility of achieving a desired chemical interaction at all depends ultimately on fundamental atomic or molecular properties and relationships which are not fully explained; considerable information can, however, be obtained (if adequate specific data are available) from thermodynamics and the use of the Nernst heat theorem. The theoretical principles at hand are not numerous, and in many cases at present their application to particular cases is difficult or unsatisfactory owing to lack of adequate determinations of various thermal and other constants; in the writer's opinion the time has by no means yet arrived to give up what may appear to be more or less empirical experimental trials in favour of implicit reliance on theoretical deductions.

2. A desired chemical change, if feasible, may proceed at too slow a rate for practical purposes, or not at all (*i.e.*, with infinite slowness). In many cases, however, the process will operate at a practical speed in presence of a catalyst.

3. In the case of solid catalysts acting on liquids or gases, the essential conditions for development of catalytic activity are :—

(i.) the presence of a surface as extended as possible, in order to give maximum mechanical contact with the gaseous or liquid phases, and characterised by an irregular structure, apparently to such an extent that a perceptible proportion of the component atoms or molecules is, as it were, thrust out of the main solid surface (*cf.* p. 21) and exposed so that part of the chemical affinity of the atom (or molecule) in question is not satisfied by the mutual attraction of neighbouring atoms (as is the case in a smooth solid surface) ;

(ii.) the presence at such a surface, whether constituting the latter *per se* or deposited upon it, of a specific chemical capable of bringing about the desired interaction.

The chief distinction between an industrial catalytic process and any other technical method, so far as the actual catalyst is concerned, lies in the care which must be taken to produce the specific active surface in the first place, and then to ensure that this surface is not materially altered under working conditions, either by exposure to too high a temperature, or by adsorption of or combination with traces of other substances which, by preventing contact between the solid surface and the interactants, act as " catalyst poisons " (*cf.* Section I., Chapter II, p. 28).

The conditions of catalyst production for any given technical process must be considered from the standpoint of the particular case. It frequently happens, for example, that the most highly active form of catalyst is not suited to a works process because it is impossible to prevent a rapid decline of activity under working conditions ; if the material forming the catalyst is abundant and relatively cheap, it is often more economical to employ a much larger quantity of catalytic agent of mediocre but prolonged activity than a special preparation of high activity, short life, and ex-

pensive to produce from the cheaper, often naturally-occurring, forms.

A good example of this is the reduced iron catalysts employed in the catalytic production of hydrogen from water-gas, or of ammonia from nitrogen and hydrogen. These are probably in many cases suitable forms of hydrated oxide of iron ores, broken to a suitable size, possibly treated with additional "promoter" substances, carefully dried and reduced without undue exposure to high temperatures (*e.g.*, not above 500°–600°). If the original ore is converted into a ferric salt, ferric hydroxide precipitated (together with "promoters" if desired) from the latter, and thoroughly washed, then dried and reduced at the lowest possible temperature, a catalytic material results which is far more active than the form in technical use; but its activity rapidly declines, owing to the contraction of surface or quasi-"sintering" effect (p. 26) which sets in at the temperature of the catalytic process. Put in another way, this implies that there is nothing to be gained by producing a catalyst surface which cannot exist unchanged at the necessary reaction-temperature. It will thus be seen that a catalyst of maximum economic efficiency and one of maximum possible activity are not necessarily synonymous terms.

Typical cases, in which natural ores or substances obtained by simple treatment of cheap existing materials form the basis of technical processes, include not only the use of treated or untreated oxides of iron in hydrogen and ammonia manufacture, but also similar catalysts used in the base metal catalytic oxidation of ammonia, and in the first stage of the Mannheim contact sulphuric acid process; in the latter the catalyst consists simply of burnt pyrites taken from the pyrites burner residues. Similarly, the iron oxide used in gas-purifiers is simply natural hydrated oxide or basic carbonate of iron, or similar material. In the case of reduced catalysts of this kind, the actual metallic catalyst is, of course, the reduced surface film of metal

resting ultimately on a " support " consisting of partially reduced or wholly unreduced oxide.

Another class of catalysts which are not deposited on a " support " of another material consists of metals in a more or less " massive " condition with an irregular surface and, in some cases, a porous or spongy internal structure. The simplest instances of this group are the platinum gauze used in the oxidation of ammonia to nitric oxide, and the copper gauze employed in oxidising methyl alcohol to formaldehyde in a current of air. It is a matter of great observation that smooth drawn metals of this type are at first sluggish in their action, but in course of use the continual production of oxide or other compounds at the surface film, followed by continual regeneration of the metal, causes the formation of an irregular, rough surface, which attains a state of maximum and constant activity. Cases in which an elemental catalyst can be directly employed in this manner are not, however, frequent. A modification of the use of originally smooth gauze is that in which a mass of fine metal turnings (" metal wool ") exposing a considerable area per unit volume, is held in a cage and coated in the first place with an attenuated film of oxide by being made to form the anode of an electrolytic cell, or by immersion in a solution of a hypochlorite ; the superficially oxidised mass is washed, dried and reduced. In this way active nickel catalysts are produced technically by means of which fats or other unsaturated liquid organic compounds can be continuously hydrogenated, the heated liquid flowing over the catalyst at a suitable temperature and meeting a current of hydrogen flowing upwards in the opposite direction. For ammonia synthesis it has been proposed to employ iron turnings oxidised electrolytically in a potassium carbonate solution, and reduced without washing (in order to retain alkali in the surface film on account of its " promoting " action on the union of nitrogen and hydrogen ; *cf.* this section, Chapter III, p. 103).

An alternative to the formation of a minute film of active material at the surface of solid metal is to produce the metal by reduction from its oxide in an extremely spongy condition, full of minute capillaries, the surfaces of which are irregular, *i.e.*, in the active state. This can be effected in the case of copper, because fused cuprous oxide is reducible at a temperature so low (250°–300°) that the resulting metal has little or no tendency to sinter. Since the density of copper is greater than that of the oxide, whilst the total volume of the mass does not shrink appreciably, the reduced metal is obtained in the form of a mass of minute interlaced rough-surfaced fibres separated by capillary spaces. The majority of fused oxides, however, are reducible only at a temperature which leads to general shrinkage and sintering of the granules. Some of the iron-alkali catalysts used in ammonia synthesis are obtained by reduction of iron oxides produced by fusion of pure iron in a current of oxygen in presence of an alkali hydroxide.

A somewhat analogous case is that of "activated charcoal," made first of all by incineration of wood fibre in such a way that the product is filled with minute interstitial pores. By further treatment of the product with air and steam at a high temperature the pore-surfaces are "activated," doubtless owing to the irregular structure produced by partial removal of carbon atoms from the original smooth surface.

The chief advantages of the catalyst materials discussed in the preceding paragraphs are ease of production on a technical scale, relative constancy of activity under working conditions, good thermal conductivity, and comparative ease of reactivation when, in course of time, they become spent owing to gradual accumulation of poisons. Deactivated metal turnings, for example, can be brought back to full activity by washing in an appropriate solvent followed by fresh anodic oxidation in an electrolytic cell; carbon, copper, and certain other of these materials are rejuvenated by

simply heating them to a high temperature for a short time in air, when toxic impurities are burnt off, and the cooled catalyst (after reduction in the case of a metal) is again obtained in an active condition.

It will be noticed, when the various industrial catalyses are described in fuller detail, that many of the actions in which catalysts of this type are used are exothermic, especially in oxidation processes. The use of a substantially metallic mass is a great advantage here in assisting in the rapid dissipation of the heat of reaction, a matter which is of vital importance in controlling the mean temperature, which must almost always be held within a relatively narrow range to obtain maximum efficiency.

The same principle applies to other exothermic processes in which, however, the actual contact agent is a metallic oxide of relatively poor heat conductivity. Examples of this are the production of acetone from acetic acid in contact with heated alumina, calcium oxide (carbonate), etc., and, especially, the controlled oxidation of aromatic compounds (*e.g.*, naphthalene or benzene) in presence of oxides of vanadium or molybdenum. Additional heat conductivity is sometimes imparted to the contact mass in such cases by distributing it in the form of a thin paste or adherent film on metallic balls or turnings; for example, the vanadium oxide catalyst is frequently mounted on aluminium granules, or on iron turnings or balls which are completely covered with a coating of aluminium.

Finally, we must consider the numerous varieties of supported catalysts in which the active component is mechanically distributed over the surface of a more or less porous, non-catalytic material in order to expose a maximum amount of active surface. The supports employed, which are usually bad conductors of heat and are chosen chiefly for their resistance to high temperature or their extreme porosity, range from broken brick and pumice through asbestos and similar

substances to highly porous or absorptive materials, such as kieselguhr, silica gels, or activated carbon. It is, of course, necessary that any compounds which hinder or " poison " the particular process shall not be present in the support used, whilst it is, on the other hand, advantageous if, *per contra*, the latter contain compounds which act as " promoters " or aids to the main catalyst.

In the oldest types of catalytic process, where mechanical dispersion of the catalyst was the primary aim, firebrick, pumice, porous tile and stone, etc., were freely employed ; thus, in the Deacon-Hurter chlorine process, firebrick impregnated with copper chloride was used, and in the earliest forms of contact sulphuric acid manufacture the platinum was deposited on purified pumice, and at a later stage on asbestos. Special fireclay has been used as a support for nickel (impregnated as chloride) in the South Metropolitan process for removal of carbon disulphide, etc., from coal-gas. Special means of producing a voluminous material have been used from time to time, for example, the platinum-magnesium sulphate catalyst in the Grillo sulphuric acid contact process, or voluminous nickel oxide produced by deflagration of a mixture of nickel nitrate and sugar, starch, etc., with or without additional inert materials.

It is in cases of actions at solid surfaces in a liquid medium that most attention has been paid to the quasi-chemical influence of the porous support employed upon the activity of the catalyst. In processes employing the liquid phase and catalyst in the form of powder, the amount of the latter is reduced to a minimum and may be of the order of 1 to 0·1 per cent. of the liquid in process. Under these circumstances, high catalytic activity becomes much more important than in continuous processes like most of those quoted in the foregoing review. The choice of support is therefore an important matter, especially since it has been found that porosity or mechanical surface is not the only factor

operative, the chemical nature of the support also influencing the activity of the catalyst. The general conditions governing the activity of such catalysts will have been gathered from the information given in Section I., Chapter II (pp. 25, 35), on the question of catalyst promoters, and here it need only be indicated that, according to the specific end in view, charcoal, kieselguhr, silica gel, etc., may in turn be found most efficient ; and that, moreover, the presence of suitable (usually minute) proportions of special promoters in the support, in addition to the actual catalyst, is frequently found to enhance the technical efficiency of the latter.

CHAPTER II

THE CATALYTIC PRODUCTION OF HYDROGEN, METHANE, METHYL ALCOHOL, AND OTHER SUBSTANCES FROM WATER-GAS AND SIMILAR GASES

Introductory.

In a description of those important modern industries which have been developed in the last few years by means of catalytic action at the surface of solid materials, attention should first be directed to the gaseous mixture which serves as primary material for a very large number of these catalyses, namely, water-gas or similar fuel gases. This is the usual starting-point in the ammonia synthesis and consequently also in that of synthetic nitric acid (from ammonia); water-gas is also the raw material for production of methyl alcohol and some higher alcohols or of other types of fuel gases, such as those rich in methane; further, it is one of the main sources of hydrogen for use in many catalytic processes such as the production of hydrogenated naphthalene or phenols for solvent or cleansing purposes, or the manufacture of hydrogenated fats for soaps, edible or other purposes (*cf.* this section, Chapter IX, pp. 208, 213). We shall therefore consider, in the first place, the production of hydrogen from water-gas or like gases by catalytic methods.

Other processes, some of which are much more widely used in various industries than the actual catalytic method, will not be referred to in detail until later. For example, the manufacturer of hydrogenated fats does not, as a rule, employ hydrogen which has been produced by the catalytic process described below; the reason for this is that hydrogen so prepared retains sufficient carbon monoxide to render necessary a special process for removal of the latter in order to

obtain hydrogen of sufficient purity for hydrogenation purposes. Consequently in this and a number of other cases alternative methods of hydrogen production are employed which yield gas of more suitable quality for the particular purpose in view.

The best hydrogen of all is that obtained by electrolysis of water, and in suitable centres where electric power is very cheap (for example, Norway, Switzerland, and parts of Italy) electrolytic hydrogen is manufactured cheaply on a very large scale, and the use of hydrogen from water-gas is eliminated. Again, where it is necessary to employ water-gas (*i.e.*, coke) as the source of hydrogen, the latter is often produced by passing steam over red-hot reduced iron ore, and when the iron has been reconverted into oxide by the action of the steam, water-gas is passed over it in order to regenerate a fresh surface of metallic iron or ferrous oxide. If this process is worked carefully the amount of carbon monoxide present in the hydrogen produced does not exceed 0·3 per cent. as compared with nearly 2 per cent. by the operation of the catalytic processes about to be described. This process, known as the Lane or Messerschmitt process, is therefore preferred by many users of hydrogen to the modern catalytic method ; as a matter of fact, of course, it is almost catalytic, since the same sequence of chemical actions which take place in the modern catalytic process is utilised, the only difference being that these are carried out intermittently and consecutively instead of concurrently.

A more general review of the alternative methods which are available for hydrogen production will be found in Chapter IX of this section (pp. 213-216), in connection with the technical hydrogenation of fats and aromatic derivatives. We now proceed to consider the catalytic production of hydrogen from water-gas and other gases, mainly in its relation to the employment of the hydrogen so obtained in the manufacture of synthetic ammonia for agricultural purposes.

The normal source of hydrogen by this method is water-gas from the ordinary blue water-gas producer, made by the action of steam on coke at about 1,200°, and consisting of 45 per cent. or somewhat more of carbon monoxide and of hydrogen, together with minor amounts of nitrogen, carbon dioxide, methane, etc. Broadly speaking, therefore, water-gas may be regarded as a mixture of equal volumes of carbon monoxide and hydrogen, and it is possible to convert this mixture into carbon dioxide and hydrogen under suitable conditions in accordance with what is known as the water-gas equilibrium :—

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

It should be added that for some purposes, especially ammonia synthesis, it is possible to employ cheaper forms of gas than water-gas, namely, various forms of what is known as producer-gas. In these cases the incandescent coke is submitted to the action of a mixture of air and steam, with the result that the gases produced consist of a mixture of hydrogen, carbon monoxide, carbon dioxide and nitrogen, the oxygen of the air present having been employed in converting a certain amount of carbon monoxide into dioxide. By suitable adjustment of the temperature of the producer and the proportion of air employed, it is possible to obtain a gas mixture which, after further passage with steam over one of the catalysts to be described, followed by removal of the carbon dioxide present, leaves a mixture of nitrogen and hydrogen in approximately the correct proportions for combination to ammonia. Alternatively, producer-gas and water-gas may be generated separately and subsequently mixed in suitable proportions.

Whilst variations in procedure of this kind may therefore be made to suit the particular nature of the use for which the hydrogen is destined, the principle of the process and also the manner in which it is carried out technically are the same in all cases, and will be

understood most readily by a description of the production of hydrogen from ordinary straight water-gas.

Catalytic Production of Hydrogen from Water-gas.

The water-gas equilibrium $CO + H_2O \rightleftharpoons CO_2 + H_2$ is dependent ultimately on the temperature of the system, and data are available from the researches of Hahn [1] and Haber for the values of the equilibrium constant "k" derived from the following equation :—

$$k = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}.$$

These are as follows :—

Temperature .	400°	500°	600°	700°	800°
k . . .	0·05	0·1	0·3	0·6	0·9

Hence it is evident that in order to obtain maximum conversion of carbon monoxide and steam into hydrogen and carbon dioxide, the equilibrium should be attained at as low a temperature as possible. The rate of attainment of equilibrium is, however, exceedingly slow at the lower temperatures and, if it were not for the fact that certain materials accelerate the change, the water-gas reaction in question would not be of technical interest. It has been known for a long time, however, that iron and related metals of the iron group possess the property of acting as catalysts for this reaction, and these metals have been used technically since about 1913 in the catalytic production of hydrogen from water-gas.

As a matter of fact, Mond and Langer [2] took out a patent in 1888 for the passage of gases containing carbon monoxide and hydrocarbons with excess of steam over heated metal catalysts, such as nickel or cobalt at about 400°, and stated that hydrogen was thereby produced. The view which they took of the mechanism of the action was that the carbon monoxide or hydrocarbons were broken up with production of

free carbon, the latter being further attacked by the steam ; for example :—

$$2CO = C + CO_2$$
$$C + 2H_2O = CO_2 + 2H_2.$$

Although, especially at higher temperatures, deposition of carbon on the catalyst itself undoubtedly takes place, it is not believed at present that this plays any great part in the hydrogen production process ; the latter is at present regarded as the operation of the water-gas equilibrium stated above, effected in practice by simultaneous oxidation of carbon monoxide and reduction of the steam by the metal-metallic oxide system, which is functioning as catalyst in the change.

A large number of patents by various groups of workers followed Mond and Langer's original patent in the course of the ensuing twenty years, but no important technical use appears to have been made of any of these until, following the work of Haber and his colleagues, the Badische Anilin und Soda Fabrik[3] took in hand the manufacture of synthetic ammonia (*cf.* this section, Chapter III). This company set itself, with characteristic thoroughness, to work out technical means of catalysing the water-gas reaction, and, in a long series of patents, published a whole variety of catalysts, temperatures and pressures by means of which it was said the process could be successfully carried out. In their first patents they emphasised the use of catalysts containing nickel, cobalt, and mixtures of similar metals, but it was evidently soon found that catalysts of this type had too active tendencies towards hydrogenation, with the result that an undue amount of the carbon monoxide present was transformed into methane, which would serve merely as a useless diluent of a gas mixture intended for use in synthesising ammonia. In later patents iron oxide[4] is generally cited as the main component of the catalyst employed, coupled with other substances intended to act as promoters, of which a wide range is given, including oxides of chromium, aluminium, thorium, zinc and

many other metals. It is probable that, in technical practice, the catalysts used at the present day consist mainly of a pure form of iron-oxide ore, perhaps stimulated by the addition of small quantities of alumina or similar material, but otherwise untreated and as free as possible from sulphur, phosphorus and similar impurities. In order to maintain a maximum surface of iron oxide for contact with the gas it is desirable not to heat the ore above 500°–600° prior to or during its use in the process. The working temperature is usually about 450°–500°, this being chosen in order to combine rapid reaction with reasonably high conversion to the hydrogen and carbon dioxide side of the equilibrium. By employing excess of steam the equilibrium is moved further over in the direction of hydrogen and carbon dioxide, and in practice, instead of employing two volumes of water-gas and one volume of steam (corresponding to the mixture $CO + H_2O$) it is usual to use about $2\frac{1}{2}$ volumes of steam per unit volume of water-gas, when the percentage of carbon monoxide left in the finished gas, after passage over the catalyst at 500°, is usually found not to exceed 2 per cent.

The process is carried out in fairly large units, consisting essentially of an internal catalyst chamber surrounded by flues, arranged in the form of heat exchangers, the temperature of the converter being maintained once the action has started by the heat developed in the reaction, namely,

$$CO + H_2O = CO_2 + H_2 + 10{,}000 \text{ cal.}$$

When starting up a converter a mixture of water-gas and air is first of all burnt in the catalyst chamber in order to raise the temperature of the unit to 500°. A mixture of water-gas and steam in the proportions indicated above is then passed over the catalyst, where it is converted as shown into a mixture of unchanged steam with a gas containing about 65 per cent. hydrogen, 30 per cent. carbon dioxide, 2 per cent. carbon

monoxide, and about 3 per cent. of nitrogen, with traces of methane. Owing to the exothermal nature of the reaction the temperature at the exit of the catalyst chamber is somewhat higher than 500° ; the emerging gases are passed through the heat-exchangers, in the other compartments of which fresh water-gas-steam mixture is passing on its way to the catalyst, and is thereby heated up to nearly 500°. The temperature of the emerging gases is thus reduced so that they leave the unit at a temperature not greatly exceeding 100°. The process thus becomes continuous and self-heating, and is efficient as regards fuel costs and charges for labour.

If water-gas (or other gas mixture) relatively poor in carbon monoxide is being passed into the converter, so that the amount of heat developed per unit volume of gas is considerably less than in the case of a straight water-gas, the temperature of the catalyst is usually maintained by mixing a suitable proportion of air with the entering gases ; a certain amount of the carbon monoxide is then burnt directly to carbon dioxide, the heat developed serving to maintain the temperature balance of the system. Owing to the absence of any external heating the water-gas consumed is practically only that required for the actual chemical action ; it is stated, in fact, that one volume of hydrogen can be produced in practice from 1·1 volumes of water-gas, as compared with one volume of water-gas theoretically necessary. So far as the yield of hydrogen from water-gas is concerned, therefore, this process is far more efficient than any of the intermittent processes to which further reference is made in Chapter IX of this section, p. 215, but on the other hand, the cost of the installation, including especially that of the elaborate purification plant necessary, makes the catalytic process suitable only for industries where hydrogen is required on an enormous scale.

It is claimed that the rate of attainment of equilibrium is notably accelerated by carrying out the pro-

cess at fairly high pressures, although, of course, it is evident that the equilibrium point itself will be independent of the pressure employed. Since, as a rule, hydrogen made by this process is destined to be used at high pressures in a further catalytic process, and since the removal (both of carbon dioxide and residual carbon monoxide) from the gas produced is facilitated by employment of higher pressures, it is convenient to carry out the whole process at, at all events, a moderately high pressure. In addition to accelerating the rate of the catalytic action the use of pressure, of course, diminishes the size of unit necessary to produce a given volume of hydrogen in a given time.

In the Badische process for ammonia synthesis discussed in the next chapter, the gas mixture employed is compressed to 220 atmospheres in five stages, namely, from 1 to 3, 3 to 9, 9 to 30, 30 to 90, and 90 to 220 atmospheres. The mixture of water-gas and steam is compressed to the 30 atmospheres stage during the hydrogen manufacturing stage, and the cooled exit gases from the converter, still at 30 atmospheres pressure, pass through tall steel cylinders 25–30 feet high and 2–3 feet in diameter, meeting therein a stream of cold water which removes nearly all the carbon dioxide. The water escapes from the base of the cylinders, its pressure is released, and the carbon dioxide is evolved and collected in dome-shaped gasholders about 35 feet high and 35 feet in diameter, which are sealed by stout leather collars lubricated by tar or mineral oil, which trickles down over the exterior of the dome. No water is employed in the storage of the carbon dioxide, which finds use in several ways in succeeding stages of the synthetic ammonia process (*cf.* pp. 107, 112).

The hydrogen is next compressed up to 220 atmospheres, and then passes into somewhat similar scrubbers containing an ammoniacal solution of cuprous salts, which serves completely to remove carbon monoxide and any carbon dioxide which has

escaped absorption in the water scrubbers. The gas leaving the ammoniacal copper scrubbers, if made from straight water-gas, will now contain about 97–98 per cent. of hydrogen, the remainder being almost entirely nitrogen. It should be pointed out that any traces of sulphur compounds present in the original water-gas are completely converted into sulphuretted hydrogen during the passage over the iron catalyst at 500°, the latter gas being, of course, removed during one or other of the scrubbing processes which follow the conversion.

The ammoniacal copper salt solution is circulated through the system and periodically regenerated by vacuum treatment, which removes all the absorbed carbon monoxide. In order to avoid undue corrosion of the vessels employed to contain the ammoniacal copper solution, it has been found advisable to ensure complete absence of any halogen. Therefore, instead of using the familiar ammoniacal cuprous chloride solution, cuprous formate or cuprous acetate free from traces of halogen is usually employed, and care is taken that a considerable excess of free ammonia is present. It is found that the observance of these conditions makes it possible to employ ordinary steel containers without serious corrosion.

Production of Hydrogen from Hydrocarbons.

Many suggestions have been made from time to time to produce hydrogen from hydrocarbons either by direct pyrogenetic action or by combination of the action of steam and high temperature. Most hydrocarbons, even methane itself, can be broken down into carbon and hydrogen by exposure to sufficiently high temperatures—1300° or above in the case of methane, and somewhat lower temperatures for other hydrocarbons such as those present in crude petroleum, acetylene, etc. The application of heat alone does not seem to be a successful technical process, nor has the exposure of a mixture of hydrocarbon vapours and

steam to a high temperature met with any technical success, although under these conditions hydrocarbons, like coke in the water-gas producer, are converted mainly into a mixture of carbon monoxide and hydrogen.

Dieffenbach and Moldenhauer [5] suggested the use of metallic catalysts such as nickel, platinum or similar metals in the form of fine wire-gauze in order to accelerate the latter reaction, and the Badische Anilin und Soda Fabrik [6] in 1913 claimed processes for the passage of mixtures of steam and hydrocarbons over catalysts such as mixtures of magnesia and nickel oxide at about 800°. Recently [7] they have described the operation of a continuous process for converting hydrocarbons and water vapour into hydrogen and carbon monoxide, in which the highly-heated gases obtained from the decomposition are cooled by contact with cold water in a type of heat exchanger ; the water thus heated is brought into direct contact with fresh gases containing hydrocarbons to be subjected to the reaction, thus heating the gases and charging them with water vapour. The resulting gas mixture is then introduced into the decomposition chamber, where carbon monoxide and hydrogen are produced. Such mixtures of carbon monoxide and hydrogen are, of course, suitable for passage with steam over an iron catalyst at 500° in order to transform them into hydrogen by the process which was described above.

The operation of the hydrocarbon process is probably very limited at present, and its utility in the future will depend entirely on the relative cheapness of coal and of suitable hydrocarbon oils as sources of the initial carbon monoxide-hydrogen mixture required for catalytic transformation into hydrogen.

Catalytic Production of Methane from Water-gas.

The heat of combustion of methane is considerably greater than that of carbon monoxide or of hydrogen, volume for volume, and many attempts have been made

to produce a commercial gas of higher calorific value than blue water-gas by partial or complete conversion of the carbon monoxide present in the latter into methane. For example, the calorific value of mixtures of carbon monoxide and hydrogen does not exceed as a rule, 300–320 B.T.U. per cubic foot, whereas a mixture of about 65 per cent. of hydrogen and 35 per cent. of methane has a calorific value of about 500 B.T.U. per cubic foot, whilst that of methane itself is, of course, still higher. A number of processes have been suggested, and in some cases put into large-scale operation, for the technical production of gases rich in methane, but so far they do not appear to have been strikingly successful, presumably because there is insufficient economic demand for gas-supplies of this type.

The suggestions which have been made for the conversion of carbon monoxide into methane may be summarised as follows :—

Sabatier,[8] who showed that carbon monoxide could be hydrogenated direct to methane at about 300° according to the equation

$$CO + 3H_2 = CH_4 + H_2O,$$

attempted to apply this reaction technically, but found that the following practical difficulties stood in the way :—

1. Presence of traces of sulphur in the original gas rapidly poisoned the catalyst.

2. If only the theoretical three volumes of hydrogen per volume of carbon monoxide are employed, a certain proportion of the carbon monoxide is decomposed according to the equation

$$2CO = C + CO_2,$$

the liberated carbon is deposited on the nickel catalyst and loss of activity results.

3. To reduce the latter difficulty to a minimum it is necessary to work below 300°, and to employ at least five volumes of hydrogen per volume of carbon monoxide. This excess of hydrogen, of course, demands a

very large consumption of water-gas per volume of methane finally produced, whilst the latter is inevitably accompanied by excess of unchanged hydrogen.

Sabatier therefore proposed to pass a mixture of water-gas and steam over a nickel catalyst at about 500°, when the carbonisation reaction indicated above takes place to a considerable extent, but the carbon is rapidly reconverted by the superheated steam into carbon dioxide and hydrogen. The operation of Sabatier's process is represented by the inventor by the following approximate equation :—

$$5CO + 5H_2 + H_2O = 2CH_4 + 2H_2 + 3CO_2.$$

It is evident that in a process such as this a number of different actions will be proceeding concurrently, of which the following may be taken as examples :—

$$2CO = C + CO_2$$
$$C + 2H_2O = CO_2 + 2H_2$$
$$CO + H_2O = CO_2 + H_2$$
$$CO + 3H_2 = CH_4 + H_2O$$
$$2CO + 2H_2 = CO_2 + CH_4.$$

Subsequently, in 1908, Sabatier suggested the use of water-gas prepared at low temperatures (containing a low percentage of carbon monoxide and a high percentage of carbon dioxide) in which the ratio of hydrogen to carbon monoxide was sufficiently great for the direct hydrogenation to proceed smoothly. Carbon dioxide was, first of all, to be removed and the residual gas passed over heated copper to remove sulphur impurities and then over nickel catalyst at about 300°.

Erdmann and Bedford [9] arrived at a similar result to Sabatier, namely, the employment of a water-gas relatively poor in carbon monoxide and relatively rich in hydrogen, by somewhat different means. They proposed to employ ordinary blue water-gas and to separate it by fractionation at low temperatures (liquid air) into (i) a gaseous portion containing from 14–17 per cent. of carbon monoxide and (ii) liquefied carbon monoxide. The carbon monoxide obtained from the

liquefied portion was employed to drive gas-engines for the liquid-air and water-gas compressors, and also for supplying necessary heat for the catalytic process. The residual gas containing about 15 per cent. of carbon monoxide and over 75 per cent. of hydrogen was found to have been very efficiently purified from sulphur compounds by the liquefaction process, and was suitable for direct passage over nickel at 280°–300°, when a gas was finally obtained containing about 60 per cent. hydrogen, 6–7 per cent. of nitrogen and 30–32 per cent. of methane, with a calorific value of about 480–490 B.T.U. per cubic foot.

Finally, it may be mentioned that Armstrong and Hilditch [10] have drawn attention to the fact that when purified water-gas alone is passed over nickel at about 250° a considerable amount of change takes place according to the equation

$$2CO + 2H_2 = CO_2 + CH_4.$$

This process is regarded as the result of two consecutive actions, namely :—

1. The ordinary " water-gas action "

$$CO + H_2O = CO_2 + H_2,$$

followed by

2. $$CO + 2H_2 + H_2 = CH_4 + H_2O.$$

If it were possible to carry out this reaction quantitatively and continuously, and to remove the carbon dioxide formed by high-pressure scrubbing with water, it is evident that this process would afford a higher yield of methane per volume of water-gas treated than any of the foregoing suggestions.

An alternative method for production of methane from water-gas is due to Vignon,[11] who has proposed the passage of a mixture of water-gas and steam over lime at 800°–900°. The main actions which are supposed to occur in this process are as follows :—

1. $4CO + 2H_2O = 3CO_2 + CH_4$
2. $2CO + 2H_2 = CH_4 + CO_2$
3. $CO_2 + 4H_2 = CH_4 + 2H_2O$

Vignon subsequently found that the same reactions occurred at a somewhat lower temperature in the actual water-gas producer if a mixture of coke and lime was employed instead of coke alone. Operating a producer filled with an intimate mixture of about 10 parts of coke with about 25 parts of quicklime heated to between 600°–800° it was found that the gas produced as a result of passage of steam consisted chiefly of a mixture of methane and carbon dioxide with small proportions of hydrogen, carbon monoxide, and other gaseous hydrocarbons. The writer is unaware, however, how far these suggestions have developed into large-scale practice.

The Production of Methyl Alcohol from Water-gas.

Until very recently the only source of methyl alcohol was the distillation of wood residues, the aqueous distillate from which contains a certain amount of methyl alcohol, acetone, and acetic and other acids. After neutralisation of the aqueous liquor with lime the methyl alcohol and acetone are removed by fractional distillation and subjected to further purification. The usual price for wood spirit is about 3*s*. 6*d*. to 4*s*. per gallon, and methyl alcohol is in fairly high demand as raw material for methylation purposes in the dyestuffs and fine chemical industries, and also, at present, as the only source of formaldehyde, which again is required in large quantities for dyestuffs, artificial resins (by condensation with phenol or urea), fine chemicals (including drugs) and as a disinfectant and antiseptic.

It has, of course, been obvious ever since Sabatier showed that carbon monoxide can be hydrogenated quantitatively into methane, that a partial hydrogenation which could be arrested at either of the stages indicated by the equations

$$CO + H_2 = H.CHO \quad \text{or}$$
$$CO + 2H_2 = CH_3OH.$$

would be of extreme commercial importance. Many attempts have been made to effect a partial hydrogena-

tion of this kind in presence of nickel, copper, and other hydrogenating catalysts, but it has invariably been found that the action either does not take place at all or proceeds almost completely to methane without production of anything more than traces of the desired intermediate products.

On the other hand, in 1913, the Badische Anilin und Soda Fabrik [12] claimed that in presence of a wide variety of catalysts, notably metals of the iron group with alkalies, zinc, zinc oxide, and other materials, ordinary water-gas was converted, at about 400°, and a pressure of over 100 atmospheres, into a complex mixture of hydrocarbons, alcohols, aldehydes and at ketones, amongst which methyl alcohol was prominent. No further progress appears to have been made in this direction, however, until about 1923, when Patart,[13] in France, stated that at high pressures and a temperature of about 400°, good yields of methyl alcohol were obtainable by passage of a mixture of water-gas and hydrogen containing one volume of carbon monoxide to two volumes of hydrogen, over a catalyst consisting of zinc oxide. At about the same time the Badische chemists appear to have returned to the attack and from this date onwards a number of patents have appeared, both by Patart and by the Badische Company, claiming the production of methyl alcohol from water-gas employing catalysts which consisted mainly of zinc oxide.

It has been stated that methyl alcohol can be produced by this process at a selling price of 1*s.* to 1*s.* 3*d.* per gallon, thus allowing ample margin for competition with wood spirit. Methyl alcohol is being manufactured by this process in Germany, France and (by Synthetic Ammonia and Nitrates, Ltd.) in England. It is difficult to obtain an estimate of the present production of methyl alcohol by these methods, but the scale of the new industry may be gathered to some extent from the statement that the Badische Company exported about 500,000 gallons of syn-

thetic methyl alcohol from Germany to America in 1925.

The conditions favouring technical success of the process can be decided to some extent from thermodynamical considerations, which show that the reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH + 27{,}000 \text{ cal.}$$

takes place in the direction of the formation of methyl alcohol most completely at a temperature of 400°–500°, and the more completely the higher the pressure. The technical feasibility of carrying out the process at the temperature indicated depends on whether a catalyst is available which will promote the change efficiently at this temperature. The use of iron-alkali catalyst induces combination of carbon monoxide and hydrogen, it is true, but, as will be shown in the final part of this chapter, these conditions tend towards the production of condensation products containing more than one atom of carbon per molecule. Patart appears to have been the first definitely to notice that zinc oxide produced methyl alcohol in good yield with a minimum of the higher by-products, so long as the temperature was not allowed to exceed about 400°.

More recent work both by Patart, the Badische Company,[14] and Synthetic Ammonia and Nitrates, Ltd.[15] has shown quite clearly that a mixture of zinc oxide and chromium oxide or, for example, a basic zinc chromate, is far more efficient than zinc oxide alone; the reason for this has become evident from work recently published by H. S. Taylor and Kistiakowsky[16] on the relative capacities of zinc oxide, zinc chromate and other compounds for adsorbing carbon monoxide, hydrogen and methyl alcohol. It is, of course, possible that combinations of metallic oxides other than zinc chromate may exist which will be found to be still more suitable in the catalysis of this particular reaction.

In technical practice, zinc chromate catalyst in granular form is charged into a converter, generally

similar in type to that employed in the synthesis of ammonia (*cf.* next chapter, p. 107). It is initially heated to 400° and subsequently maintained at the reaction temperature by the exothermic nature of the change and an efficient system of heat-exchangers between the treated and untreated gases. The gas employed may be a mixture of carbon monoxide and hydrogen in the relative proportions of one volume of the former to two of the latter, or water-gas alone may be employed, according to Patart, in which case about half of the carbon monoxide present will be left uncombined and the residual gas has an appreciable fuel value. It is also possible to use any gas, at least one-third of which is composed of a mixture of carbon monoxide and hydrogen, but of course the speed of the reaction is not so great as in the case of ordinary water-gas. The plant is run at a temperature of 350°–400° and a pressure of 150–250 atmospheres; the exit gases from the plant are passed under pressure through a condensing system in which nearly all the methyl alcohol is removed, the residue being recovered if necessary by scrubbing through water. Simple distillation of the crude methyl alcohol furnishes the pure product.

It is claimed that, on the basis of the water-gas consumed, one part of methyl alcohol can be obtained from two parts by weight of carbon, whilst the yield of methyl alcohol per ton of coal originally used should be not less than 400 kg. The zinc oxide-chromium oxide catalysts at present used are said to maintain their activity for prolonged periods, and the output of methyl alcohol from the Patart plant unit is about 150–200 kg. per day. In the production of methyl alcohol by this method the chief precautions necessary appear to be the complete elimination of all traces of sulphur compounds from the gases passed into the converter, together with the absence from the catalyst and the catalyst chamber of any trace of iron, nickel or cobalt, which tend to induce undesired

hydrogenating actions leading to the formation of methane.

The suggestion has recently been put forward[17] that if methyl alcohol synthesis from water-gas can be carried out in small units, water-gas plant in the town gas industry, which is comparatively idle in summer, might be employed at this season in the preparation of methyl alcohol or, alternatively, of the other liquid fuel products described below. Apart from the technical possibilities or otherwise of operating in small units, it is doubtful whether seasonal production of methyl alcohol and "synthol" in this way would prove able to compete with the steady output of a large plant designed solely for the production of these chemicals.

Production of "Synthol" and Liquid Fuels from Water-gas.

It has been mentioned that the earlier patents of the Badische Anilin und Soda Fabrik[18] in 1913 described the formation of a mixture of liquid hydrocarbons and oxygenated products from water-gas at high pressures and temperatures in presence of iron-alkali catalysts. About 1923 F. Fischer[20] and his collaborators examined this reaction further, with a view to obtaining substitutes for petrol from water-gas. Concurrently, the Badische Company,[18] and also Patart[19] in France, appear to have resumed the study of the action of iron-alkali catalyst on water-gas at high temperatures; the object was to obtain, instead of methyl alcohol, either a mixed hydrocarbon-alcohol, etc., product, suitable for fuel for internal combustion engines, or definite technically useful alcohols somewhat higher in the series than methyl alcohol.

The large-scale operation of this process would presumably be effected in vessels similar in type to those described for methyl alcohol, but the catalyst, instead of being mainly composed of zinc oxide, would consist of reduced or partly-reduced metals of the iron group, impregnated before reduction with an

alkaline solution containing, for example, potassium or sodium carbonate, lime or baryta. An enormous number of alternative, and in many cases complex, mixtures of various oxides and metals have been suggested by the three groups of workers mentioned and other investigators, but it seems certain that for technical purposes a reduced iron catalyst containing small amounts of free alkali is substantially all that is required. The temperature of reaction is 400°–500° and the pressure used is from 100–200 atmospheres.

Various explanations are offered at present of what goes on in this somewhat complicated series of reactions. Fischer's view is that carbides of the iron metals present are produced initially, and that these are decomposed in presence of hydrogen to form nascent methylene groups which may polymerise or, in addition, may combine further with hydrogen so that saturated hydrocarbons are produced. On this theory the concurrent formation of oxygenated compounds would presumably be explained by interaction between the nascent methylene compounds and methyl alcohol formed simultaneously from carbon monoxide and hydrogen. Other workers have put forward explanations of the process which do not necessarily involve the production of carbides at the surface of the metal: for example, it may be supposed that the following sequence of reactions might take place :—

(1) $CO + 2H_2 = CH_3.OH$
(2) $CH_3.OH + CO = CH_3.COOH$
(3) $CH_3.COOH + H_2 = CH_3.CHO + H_2O$
(4) $CH_3.CHO + H_2 = C_2H_5.OH$
(5) $2CH_3.COOH = (CH_3)_2CO + H_2O + CO_2$
(6) $(CH_3)_2CO + H_2 = (CH_3)_2CH.OH.$

The interaction between carbon monoxide and methyl alcohol is known to be favoured under high pressure by the presence of alkalies, resulting in the production of the corresponding acid. The sequence of actions from acetic acid to ethyl alcohol may be considered as possible in the presence of a hydrogenating

catalyst, but the first stage is not very likely to occur to any extent. The alternative scheme from acetic acid *viâ* acetone to isopropyl alcohol is perhaps more likely to take place. As a matter of fact, ethyl alcohol does not appear to be present in any quantity in the " synthol " products. It is obvious, however, that the substances which may reasonably be supposed to be present in contact with an iron-alkali catalyst, can, by the combined specific actions of the alkali on the one hand and the hydrogenating action of the iron on the other, give rise to a multitude of chemical compounds of the types indicated.

Little information is available as to the actual composition of various forms of " synthol " produced by the Badische Company or by Fischer, but in one example in which the oxygenated compounds preponderated, there was 2 per cent. of hydrocarbons present, the remainder of the organic materials consisting of a mixture of alcohols, aldehydes, ketones, and acids containing up to 9 carbon atoms per molecule. This complex mixture distilled between 60° and 200°. Another of Fischer's products, consisting mainly of hydrocarbons, distilled (to the extent of 96 per cent.) between 40° and 130°, a small amount of gaseous hydrocarbons and also of residual high-boiling petroleum light products being also present.

A recent patent by Patart (E.P. 250,563/1926) gives a comprehensive description of the manufacture of " synthol " by passage of water-gas at high pressures over a mixed catalyst at 320°–400°, and describes the fractional condensation of all liquefiable products, including carbon dioxide, together with a suitable plant for carrying out the whole cycle of operations continuously. Apparently the reaction

$$14CO + 16H_2 = 2C_5H_{11}OH + 4CO_2 + 4H_2O$$

is aimed at as representing the most desirable end product, but a mixture of higher alcohols is, of course, obtained in practice.

The higher alcohols containing 4, 5, 6 and 7 car-

bon atoms have been isolated from various "synthol" products, and it would appear that in each case they belong to the *iso*- or branch-chain series of alcohols.

So far, although much has been published regarding the possibilities of the synthol process in the direction of providing cheap synthetic fuel or of producing useful solvent alcohols containing from 4 to 7 carbon atoms per molecule, it does not appear to have been worked on more than a semi-technical scale. It is therefore somewhat difficult to judge its potentialities. It seems doubtful, taking for example Fischer's estimate of a total yield of 100 grams of hydrocarbons from each cubic metre of water-gas, whether the hydrocarbon mixture could compete economically with either ordinary petrol, or with the liquid fuel which is obtained on a practical scale by the Bergius process for the "hydrogenation" of coal itself. Again, considering the modification of "synthol" which consists mainly of alcohols and other oxygenated compounds, although Patart estimates that a yield of 1 kg. of isobutyl alcohol could be obtainable from 3 kg. of coal, it appears doubtful whether any given individual alcohol could be produced technically at economic values by this process.

There are several alternative sources of these alcohols: for example, butyl alcohol by fermentation of starch, isopropyl alcohol from acetone; whilst a number of them can be produced by hydration, in presence of sulphuric acid, of various olefinic hydrocarbons present in various commercial oil gases such as natural gas, cracked-oil gas, and coke-oven gases.

It remains to be seen, therefore, how far the "synthol" process will make headway against these alternative processes; so far, however, as the straight synthesis of methyl alcohol described in the preceding section of this chapter is concerned, there is no doubt that this marks an outstanding advance in the provision of a new and cheap source of methyl alcohol and consequently of formaldehyde.

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CHAPTER III

THE INDUSTRIAL SYNTHESIS OF AMMONIA AND OF UREA

The Economic Side of the Fixed Nitrogen Problem.

It is self-evident that the provision of adequate supplies of food for the increasing population of the world is as important a problem as any which confronts us, and in consequence the processes which form the subject of this and the succeeding chapter, owing to their far-reaching influence on the solution of the food supply problem, are more vital than any other methods of industrial catalysis.

With the exception of the *Leguminosæ*, growing vegetation is not able directly to convert the nitrogen of the air into combined nitrogen which can be utilised to elaborate the protein of plants. Nitrogen must be present in the soil in the "fixed" condition both as ammonium compounds and as nitrates, and the more intensively the soil is exploited the more necessary it becomes to replenish the stock of fixed nitrogen therein. To a certain extent this has long been done by growing legumes, by applying animal manures, and by ploughing under green crops ("green manuring"), but these measures do not as a rule suffice, and have been supplemented for nearly a century by the use of increasing amounts of artificial fertilisers, such as ammonium sulphate or nitrate of soda.

Until comparatively recent times, the sources of these materials were on the one hand by-product sulphate of ammonia, isolated from crude coal or coke-oven gas during purification, and on the other hand, natural sodium nitrate obtained from the deposits of this material in Chile.

The fundamental problem has recently been stated very clearly by Lt.-Col. G. P. Pollitt [2] as follows :—

"There is a very direct connection between the increase in the world's population and the world's requirements of fixed nitrogen.

It may be estimated that for at least 500,000 years a human being differing very little from his present form has inhabited the earth. In all that time up to 1800 A.D., the world's population has increased from its beginnings to a figure estimated at 800 millions. In the next 100 years from 1800 A.D. to 1900 A.D. it rose to 1730 millions, that is, it more than doubled itself, and this rate of increase, or something approaching it, is continuing to-day. This rate obviously cannot be continued indefinitely under any circumstances ; it cannot go on at all unless the productivity of the soil keeps pace with it."

The development of fresh tracts of virgin soil in all parts of the world will, in due course, reach its limit, and the only method then available will be to increase the output per unit of agricultural land, that is to say, to increase very largely the use of inorganic fertilisers, a most important constituent of which is fixed nitrogen. This was already apparent to Sir Wm. Crookes[1] thirty years ago when, in a famous address to the British Association in 1898, he emphasised the absolute necessity for preserving and adding to our nitrogen resources, and stated that the fixation of atmospheric nitrogen was one of the great discoveries awaiting the ingenuity of chemists.

This address certainly stimulated the search for commercial methods of producing ammonia or nitric acid from the atmosphere, although a certain amount of laboratory investigation on the production of ammonia from nitrogen and hydrogen, either by the electric arc or by passage over metals such as titanium or iron, had already been carried out by Deville[3] (1865), Tessié du Motay[4] (1871), Tellier[5] (1881), Le Chatelier[6] (1901) and others.

About 1904 Birkeland and Eyde[7] worked out conditions under which, given sufficiently cheap electric power, air could be directly and economically converted into oxides of nitrogen by passage through an electric arc, a process which, though comparatively simple, involves a power consumption of about 65,000 kilowatt-hours per ton of nitrogen fixed. A little later, the fixation of nitrogen by combination with calcium carbide to give cyanamide was worked out

technically by Frank [30] and Caro,[31] and this process (which is again referred to at the end of this chapter) has met with much success. It has become apparent, however, within the last fifteen years that the cheapest and most economical process of nitrogen fixation is the combination of nitrogen and hydrogen at high pressure in presence of a suitable catalyst, forming ammonia, followed if desired by catalytic oxidation of the ammonia to oxides of nitrogen (nitric acid).

Before proceeding to describe the catalytic processes of ammonia synthesis it is not out of place to give a few statistics showing the development of the fixed nitrogen industry, and of the manner in which catalytic synthetic ammonia plants are springing up at the present time.

Roughly speaking, if we take 1910 as a date immediately prior to the initiation of the synthetic-ammonia processes, we find that, expressed as tons of nitrogen in the combined state, the world production for that year was 206,000 tons in the form of by-product sulphate, and 382,000 tons as Chile nitrate, whilst in 1903, the total production from both sources was about 340,000 tons. In 1925 and 1926 the world production of nitrogen was estimated as follows :—

	Tons (of Nitrogen).	
	1925.	1926.
By-product ammonia . . .	343,500	328,000
Chile nitrate	391,200	312,500
Synthetic ammonia	401,600	460,300
Cyanamide	166,300	198,000
Nitrate of lime (arc process) . .	37,500	33,000
Guano and nitrate of potash . .	15,300	10,700
	1,355,300	1,342,500

In 1926 the total world consumption of nitrogen for all purposes was 1,400,000 tons, and the demand for fixed nitrogen has, in recent years, been increasing at

an approximate compound rate of 11 per cent. per annum.

Some idea of the rate at which the synthetic ammonia process is being developed in various countries may be gathered from the following table of approximate annual outputs at the present time (1927) :—

Country.	Process.	Tons per Annum as Fixed Nitrogen.
Germany . . .	Haber-Bosch . .	400,000
England . . .	Billingham . .	60,000
Italy . . .	Casale and Claude .	12,000
France . . .	Casale . . .	6,000
Belgium . . .	Casale . . .	6,000
Japan . . .	Various . . .	6,000
Spain . . .	Casale and Claude .	5,000
United States . .	Various . . .	4,500

It should be noted that the full potential output of plants, the construction of which was in hand at this date, is in most of these countries considerably greater than the figures given ; so that the production of synthetic ammonia by catalysis is being increased at an enormous rate. Britain is at present second only to Germany (although very far behind her) in actual output of synthetic ammonia.

Theoretical Aspects of the Synthetic Ammonia Process.

The synthetic ammonia process depends ultimately on the equilibrium point attainable in the change

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

At the time of the earlier attempts to produce ammonia in the presence of metals referred to above, the equilibrium data could at best be determined empirically ; with the help of Nernst's heat theorem it has become possible, given a number of experimental determinations at various temperatures and pressures, to calculate the composition of an equilibrium mixture over an extended range of temperatures and pressures. This

was first carried out in the case of the ammonia equilibrium by Haber [8] and Le Rossignol [9] and co-workers,[11] followed by Nernst and Jost,[12] experimental values being obtained over a range up to 70 atmospheres. More recent determinations of the ammonia equilibrium were made by Larson and Dodge [13] in 1923 and 1924, covering a range of pressures from 10–1,000 atmospheres and a wide range of temperatures. The Haber and Nernst figures for the lower range of pressures were satisfactorily confirmed. The nature of the technical problem will be gauged when it is said that at 100 atmospheres pressure the percentage of ammonia in the equilibrium mixture ranges from 80 at a temperature of 200°, through 25 at a temperature of 400°, 10·4 at 500°, 4·5 at 600°, 1·1 at 800° to 0·44 at 1,000°, whereas the rate of establishment of equilibrium falls to a very small value as the temperature decreases. The following table gives the percentage of ammonia at equilibrium over the temperature range 350°–500° for pressures from 1–1,000 atmospheres.

Per Cent. NH_3 in Equilibrium Mixture.

Pressure (atm.).	1	10	30	50	100	200	300	400	1,000
Temp.									
350° .	—	7·37	17·80	25·11	—	—	—	—	—
375° .	—	5·25	13·35	19·44	30·95	—	—	—	—
400° .	0·44	3·85	10·09	15·11	24·91	36·3	—	—	—
425° .	—	2·80	7·59	11·71	20·23	—	35·5	53·6	69·4
450° .	—	2·04	5·80	9·17	16·36	—	—	—	—
475° .	—	1·61	4·53	7·13	12·98	—	31·0	47·5	63·5
500° .	0·13	1·20	3·48	5·58	10·40	17·6	26·2	42·1	—

Prior to the work of Haber and Le Rossignol no means were known of attaining the equilibrium in a technically useful time at temperatures below about 800°, at which it will be seen the conversion to ammonia is extremely small. They proceeded to search for and to discover materials which would promote the more

rapid attainment of equilibrium at considerably lower temperatures, that is as low as 400°–500°. Thereby they rendered a service greater even than their equilibria data, and paved the way for modern practice.

It is, perhaps, unnecessary here to go more deeply into the purely theoretical side of the ammonia synthesis, except to point out that under working conditions a higher output of ammonia can usually be obtained by not allowing the gases to remain in contact with the catalyst sufficiently long for complete attainment of equilibrium. In other words, in accordance with the law of mass action the later stages of approach to equilibrium proceed much more slowly than the initial part of the conversion of the nitrogen-hydrogen mixture to ammonia, so that, if the rate of passage of the gas mixture is increased, for example, ten times, this may very well result in, say, half the amount of ammonia being produced at any given passage of the gas at the higher rate of flow compared with that at the lower rate ; but it is obvious that even so, in a given time five times as much ammonia would actually be produced at the higher rate of flow than at the lower. Haber and Greenwood [10] give data for ammonia output in presence of a uranium carbide catalyst at 515° and 114 atmospheres pressure, which illustrate this point.

Space-time-yield of Ammonia at 515° *and* 114 *Atmospheres* (*Haber and Greenwood*).

Litres gas per litre catalyst space per hour .	5,800	31,650	82,600	194,000
Percentage of ammonia (volume) produced .	7·63	6·42	4·78	4·18
Kg. ammonia per litre catalyst space per hour.	0·318	1·46	2·84	5·83

The general conclusions to be drawn from the theoretical work which has been carried out on this problem, therefore, assume the following form :—

(1) The conversion of a nitrogen-hydrogen mixture

to ammonia becomes relatively high at pressures of the order of 1,000 atmospheres, and is sufficiently high for technical success from about 100 atmospheres pressure onwards, at all events at temperatures from 600° downwards.

(2) Formation of ammonia is favoured by low temperature, but in the absence of catalysts the attainment of equilibrium is exceedingly slow even at high temperatures (800°–1,000°), at which, in any case, the percentage of ammonia at equilibrium is too small to be of practical interest.

(3) The attainment of equilibrium can be accelerated to a marked degree by the employment of appropriate catalysts which, as at present understood, are active from about 400° upwards.

These principles have been applied technically in various ways, and a description of the various synthetic ammonia processes now in operation consists essentially of an account of these variations.

Catalysts Employed in the Synthesis of Ammonia.

Haber and his co-workers studied the action of a variety of metallic catalysts and apparently favoured osmium and uranium as the most active catalysts; iron, nickel, manganese and other metals of the seventh and eighth groups of the Periodic System were also found suitable. In actual practice the rarer metals mentioned have been found unsuitable either on the score of cost or because of their susceptibility to catalyst poisons, and the basis of most of the catalysts in use at the present day is probably pure iron. At the same time it has become evident that the addition of small amounts of alkaline materials greatly stimulates the action of the iron catalyst, and many patents have been taken out for the production of different types of iron-alkali catalysts.[14] Thus it may be mentioned that whilst Casale[15] advocates that the iron should be prepared by fusion of pure iron turnings with an alkaline-earth oxide (lime) in a current of oxygen,

followed by subsequent reduction of the iron oxide formed, Collett and Synthetic Ammonia and Nitrates, Ltd.[16] recommend the fusion of 160 parts of pure ferric oxide with 56 parts of lime at 1,200°, followed by reduction of the calcium ferrite thus formed. Again, Lush,[17] in a recent patent, employs anodic oxidation of pure iron turnings in a bath of potassium carbonate (on similar lines to his fat-hydrogenation catalyst, *cf.* this section, Chapter IX, p. 221), followed by reduction of the catalyst without washing away the adherent alkaline carbonate.

The function of the catalyst in the ammonia synthesis has been studied from the point of view of adsorption,[18] and it is clear that as usual a material which acts as a catalyst for the production of ammonia must possess a capacity for selective adsorption of both hydrogen and nitrogen. The amount of adsorption has been shown to be considerably increased in presence of the alkali, although the precise function of this or any other catalyst promoter is still by no means clearly understood. Kunsman [19] has recently compared the thermionic emission and the heats of activation of pure iron and iron-alumina-alkali catalysts, and finds that the emission of positive ions and the heat of activation are greater in the case of the more active composite catalyst; he concludes that the primary effect of the promoter is to increase the number of atoms at which catalytic action takes place.

Technical Sources of Hydrogen and Nitrogen for the Ammonia Synthesis.

In commencing to describe the actual technical procedure involved it may be useful to consider first of all, from a general standpoint, the relative merits of different sources of hydrogen and nitrogen. It is generally considered that when hydrogen from water-gas is used, 60 per cent. of the final cost of the ammonia lies in the production and purification of

the hydrogen required ; the present cost of ammonia by the catalytic process is probably somewhere in the region of £20 per ton (as NH_3). In spite of the apparent high cost of hydrogen from water-gas (coal), electric power has to be very cheap before the cost of electrolytic hydrogen can compare with the former type, but in a number of installations, chiefly in Italy, France and Spain, it has been found possible to use this type of hydrogen (which, for catalytic purposes, is always purer than water-gas hydrogen). An alternative source of hydrogen suggested by Claude [21] is coke-oven gas. Dodge has examined this suggestion critically from the point of view of cost, and concludes that hydrogen can be prepared from coke-oven gas by thermal decomposition of the hydrocarbons present at a high temperature followed either by liquefaction of the carbon monoxide present, or by removal of the latter by the water-gas catalytic process. The cost of production of hydrogen by either modification of this process would apparently be much the same, but Dodge [22] considers that it is doubtful whether hydrogen so produced would pay its way unless the process was combined with preliminary removal of olefinic constituents of the gas and conversion of the latter into alcohols of technical value.

At present, therefore, the choice appears to rest almost entirely between water-gas hydrogen and electrolytic hydrogen. As regards the nitrogen required, which it will be noticed forms only 25 per cent. of the total mixture of gases, this was originally produced by fractional distillation of liquid air, the nitrogen obtained being mixed off with the hydrogen. Present-day practice, however, consists more frequently in the employment of a mixture of water-gas and producer-gas in the water-gas hydrogen catalytic process, or of these two gases with air, in suitable proportions to lead finally to a mixture of nitrogen and hydrogen in the necessary ratio. It has been

stated that this process can be so far controlled as to produce the mixed gases continuously in the desired proportions, and in any case it is obvious that slight variations in the proportions of the gases can be compensated for by collection in a series of holders and appropriate mixing off. By this means the necessity for a separate liquid air plant is eliminated.

Finally, in one of the processes about to be described, in which electrolytic hydrogen is mainly employed,[25] the necessary nitrogen is obtained by oxidation of a portion of the ammonia output with air as described in the next chapter, p. 123, forming nitric acid; the residual nitrogen from the air employed in oxidising the ammonia, which amounts to about 5 volumes of nitrogen for every volume of ammonia oxidised, provides ample supplies for the synthesis of further quantities of ammonia. Another procedure [26] is to burn a mixture of air and hydrogen under the boilers used for raising steam, condensing the water for electrolysis and using the residual nitrogen for admixture with hydrogen.

Technical Processes in Use for Combining Nitrogen and Hydrogen.

There are five main types of process, namely, the Badische Anilin und Soda Fabrik (Haber-Bosch), the Synthetic Ammonia and Nitrates (Billingham), and the Fauser, Casale and Claude processes. These will be briefly discussed in this order, and it will be gathered that the chief differences between them are in the pressures employed, the source of the hydrogen and nitrogen, and the means adopted for the removal of the ammonia produced.

(1) *The Badische Synthetic Ammonia Process.*[24]—The gas mixture is manufactured in a water-jacketed gas producer by the action of a mixture of steam and air on coke in such proportions that, after submission to the catalytic hydrogen process, the composition of the gas is approximately 25 per cent. nitrogen and

75 per cent. hydrogen. The gases are compressed in five stages to 220 atmospheres, namely, from 1 to 3 to 9 to 30 to 90 and finally to 220 atmospheres. Carbon dioxide is removed at the 30 atmospheres stage by scrubbing with water; the gas is then compressed up to 220 atmospheres and the carbon monoxide removed, as described in the preceding chapter, p. 83. The purified nitrogen-hydrogen mixture is passed through a series of small catalyst chambers to remove catalyst poisons, and is then circulated rapidly through the main ammonia converters, a yield of about 8 per cent. of ammonia being obtained at each passage.

The converters consist of cylinders 20 ft. high and 2 ft. in diameter, constructed of special steel enclosing an internal vessel of ordinary mild steel $\frac{3}{8}$–$\frac{1}{2}$ inch thick. In course of time the internal lining becomes decarbonised by the hydrogen and permeable to the latter gas, and in order to prevent accumulation of gas between the internal and the external cylinders, the latter are drilled throughout their length at a pitch of 9 inches with $\frac{3}{16}$ inch holes. Each cylinder is placed in a separate compartment on one side of a heavy concrete wall, on the other side of which are ranged all the gas and temperature controls. The flow of gas is adjusted continuously (and mainly automatically) by meters of the Venturi type, and the temperature control is also largely automatic, the catalyst being so packed in the converters that the process is carried on by the slight heat developed in the reaction. The interior of the converters is maintained at 550°–600°, and the exterior of the shell at about 300°–400°. The exit gases, still at the pressure of 200 atmospheres, are scrubbed through water and the wash water is released through a thick glass tube supported in a slotted steel pipe; the ammonia solution is converted into sulphate by adding carbon dioxide and stirring the ammonium carbonate liquor with a suspension of gypsum or anhydrite, as described

below. Sufficient hydrogen and nitrogen are dissolved in the water at the high pressure employed to make it worth while to scrub the gases, released when the water is brought to atmospheric pressure, through a water tower which removes ammonia from the recovered nitrogen and hydrogen, the latter being re-circulated over the catalyst.

As the nitrogen and hydrogen are removed from the gas mixture the amount of inert hydrocarbons, etc. (originally small) becomes sufficiently great to retard the process and from time to time these are drawn off and employed as fuel.

The whole process is largely controlled automatically and requires a minimum of manual supervision. The first of the Badische plants was erected at Oppau in 1911–1912 and came into operation shortly before the outbreak of war, 1914, with an output of 130,000 tons of fixed nitrogen per year; in 1917 an additional plant was erected at Merseburg with an ultimate output of 350,000 tons of fixed nitrogen per year.

(2) *Synthetic Ammonia and Nitrates* (*Billingham*).—The British plant operated by this company, which is a subsidiary of Imperial Chemical Industries, Ltd., has been developed on the lines of the original Haber process, but apart from the indications afforded by the patent literature, details of the process employed have not been made public. It has, however, been stated that the company's experts are satisfied that the alternative methods described below do not offer any advantage under English conditions over the general scheme of the Haber process, the latter having been modified and adapted to the local conditions. The nitrogen-hydrogen mixture is obtained from producer-gas as in the Badische process; the working of the ammonia converters is on somewhat similar lines, and at present the bulk of the ammonia produced is converted into sulphate by interaction of ammonium carbonate and calcium sulphate, the latter being obtained from a large deposit of anhydrite situated

near the site of the works on Teeside. Although the general principles of the Haber-Bosch method have been employed at Billingham as the foundation of the process, it is understood that many alterations in detail have been made, especially as regards plant construction ; the efficiency of the Billingham plant is said to mark a considerable improvement over that of the original German plants.

(3) *The Fauser and Casale Processes*.—These modifications of the original Haber-Bosch process may be considered together because their main difference is the use of somewhat higher pressures in the ammonia converters, namely, from 300–500 atmospheres. Various other differences in operation will be observed, but these usually arise from economic factors which, for example, render modifications in the production of the original nitrogen-hydrogen mixture desirable. These processes appear to be coming into operation in Italy, Switzerland and France, together with some other countries, but do not seem to be making headway either in England or Germany.

The Fauser [25] process is concerned with the conversion of electrolytic hydrogen into ammonia, so that simultaneous production of nitrogen from producer-gas becomes impracticable. A small plant for the catalytic oxidation of ammonia to nitric acid is therefore added to the main ammonia plant, and in this a certain proportion of the ammonia output is mixed with air and converted to nitric acid. The residual gases from the nitric acid scrubbers consist mainly of nitrogen with small amounts of unused oxygen ; these are mixed with hydrogen and passed over heated platinised-asbestos, when all the oxygen is converted into water and the purified nitrogen is ready for mixing with electrolytic hydrogen and passage through the ammonia converters. As already stated, one volume of ammonia furnishes in this way five volumes of nitrogen, which, in turn, are ultimately capable of producing 10 volumes of ammonia, so that

theoretically it is only necessary to oxidise 10 per cent of the ammonia output in order to obtain sufficient nitrogen from the air for production of the total ammonia output required. The ammonia converters are somewhat similar to those used at 200 atmospheres, allowance, of course, being made for resistance to the higher pressures employed, and for the fact that less space is required for the production of a given amount of ammonia in a given time at the higher pressures. In the Fauser process the exit gases are submitted to refrigeration and a considerable proportion of the ammonia removed in the liquid state, that remaining being scrubbed with water as in the other systems.

The Casale process [26] is also designed mainly for the use of electrolytic hydrogen. Nitrogen is obtained by burning the oxygen of the air with hydrogen, and the water formed is condensed and used in electrolysis, which requires particularly pure water. The chief characteristic of the process, however, is said to be the introduction and maintenance of a certain percentage of ammonia in the nitrogen-hydrogen mixture. The ammonia prevents overheating of the catalyst as equilibrium is established at the catalyst surface, and this tends to reduce the working temperature, and to maintain a higher conversion than if the temperature were allowed to rise locally ; it also increases the specific heat of the gas mixture, thus contributing to efficient heat interchange. The Casale method of preparing the catalyst has already been mentioned above ; the process is designed to work at 300–500 atmospheres and about 600°, and is otherwise very similar in operation to the Fauser process.

(4) *The Claude Process.*[27] This process works at 900–1,000 atmospheres, that is, at much higher pressures than any of the preceding methods ; the advantages claimed are speed of conversion in the actual combination, small size of plant required for a given output, rapidity of starting up the plant, and, finally, it is stated that the Claude plant is the only one which

is suitable for the production of comparatively small quantities of ammonia—for example, for small units giving about 5 tons per day of fixed nitrogen. The principle of the process is exactly similar to that of the Haber-Bosch method except for the difference in pressure. Either water-gas or electrolytic hydrogen may be employed and Claude has also suggested processes for the recovery of hydrogen from coke-oven gas for use in the ammonia synthesis.

The amount of ammonia formed per hour per litre of catalyst space is stated to be 5,600–6,700 gm. by the Claude system as against 350–400 gm. by the Haber process, in consequence of the much higher percentage of ammonia at equilibrium at 1,000 atmospheres. Similarly, the heat evolved by the reaction is also much greater per unit of converter space, and consequently it is possible to use quite small vessels without encountering difficulties in radiation losses. The Claude catalyst tubes are of high tensile alloy, cast solid and bored out and the customary peroxidised-iron catalyst is used. The gas mixture is passed through four sets of catalyst tubes, traversing the first two in parallel, the gas streams being then united and passed in series through the second pair of tubes; ammonia is removed from the reacting gases by cooling between each passage over the catalyst. Starting all cold, a Claude plant will begin to produce ammonia in between 4 and 5 hours, whereas the Haber system requires three days.[28]

The apparent difficulty of compressing the gases to and circulating them at such extremely high pressures, owing to leaks at joints and valves, is more than compensated for by the fact that, owing to the high pressure, the pipe connections, etc., need only be of relatively small diameter, and consequently it is much more easy to render joints and valves effectively gas-tight. Finally, 97–98 per cent. of the ammonia produced can be removed in the liquid state by simple water-cooling of the exit gases from the converters, and it

only remains to absorb the residual 2–3 per cent. of unliquefied ammonia in sulphuric acid. In spite of the advantages claimed for the system, however, it does not appear up to the present to have come into such general use as those operating at lower pressures.

Combination of Ammonia as Solid Salts for Marketing.

As already indicated, the bulk of the synthetic ammonia produced is converted into sulphate. At first this was effected similarly to the production of by-product sulphate of ammonia, namely, by direct neutralisation of the ammonia with dilute sulphuric acid followed by crystallisation. It was soon realised, however, that the use of free sulphuric acid was an extravagance, for by combining the ammonia produced with carbon dioxide (usually available as a by-product in the manufacture of the hydrogen required) it is possible to produce ammonium sulphate by double decomposition with a suspension of calcium sulphate :—

$$(NH_4)_2CO_3 + CaSO_4 = (NH_4)_2SO_4 + CaCO_3.$$

As calcium sulphate occurs fairly abundantly in the form of gypsum and anhydrite, this procedure has become general both in Germany and in England—the site for the main British works having, in fact, been chosen partly in consequence of nearness to a large deposit of this mineral.

Sulphate of ammonia, however, is by no means the only form of fixed nitrogen which is desired by the agriculturalist, and other forms of so-called compound fertilisers have also to be taken into account. An important matter is the provision of nitrate fertilisers in substitution for sodium nitrate and for this purpose ammonia is oxidised to nitric acid, the latter being further combined with ammonia to form ammonium nitrate ; a mixture of the latter with chalk (by-product calcium carbonate), termed nitro-chalk, is another of the modern forms of fertiliser. The Germans, in

order to overcome the deliquescent properties of ammonium nitrate, manufacture a double nitrate and sulphate of ammonia, but the stability of this material, especially when stored in bulk, is uncertain, and had some connection with the disastrous explosion at Oppau in September, 1921. Again, phosphates are necessary ingredients of many agricultural fertilisers, and a certain amount of ammonia is converted into ammonium phosphate by double decomposition of the carbonate with calcium phosphate, or by direct combination with phosphoric acid produced from arc-process phosphorus. To a smaller extent, ammonium carbonate itself is required for certain purposes.

The plant necessary for converting ammonia into any of these solid salts is more or less standardised in type, and consists of agitators for effecting the double decomposition, followed by settling or filtration and concentration of the clear liquor to crystallisation in double or triple-effect vacuum evaporators.

The Catalytic Production of Urea.

Many people hold the opinion that nitrogen can be more efficiently supplied to the soil in the form of urea, $CO(NH_2)_2$, than as ammonium salts. It is considered that nitrogen can be assimilated by the plant most readily when it is combined simply with carbonic acid, but ammonium carbonate or carbamate are dissociated too readily into ammonia and carbon dioxide to permit them to be efficient conveyers of ammonia to the soil.

Urea, first synthesised by Wöhler exactly 100 years ago, has only lately been prepared on an industrial scale; over 9,000 tons of it were made in Germany in 1926–1927, and it is understood that other countries are planning its manufacture. Theoretically, urea should be an ideal source of nitrogenous plant-food; practically, it may be said not to have come quite up to expectations. It has given excellent results on grassland, in garden and glasshouse, and also on

rubber plantations in Southern India, where it has proved very successful as an antidote to the disease of rubber trees known as "Secondary Leaf-Fall." It is, moreover, very concentrated, containing 46 per cent. of nitrogen, and is thus economical in use and transport. Unfortunately, however, urea, being readily soluble in water, is leached out of arable soils almost as readily as sodium nitrate; it is also hygroscopic and therefore difficult to store in humid climates. Further, experience has shown that it does not mix well with superphosphate or low-grade potash salts.

Urea is obtained technically either from calcium cyanamide or by direct union of ammonia and carbon dioxide.

The Cyanamide Process.—After calcium carbide became a commercial product, about 1895, attempts were made to utilise it as a basis for fixing atmospheric nitrogen. Between 1904 and 1908 large-scale plants were put into operation by Frank [30] and Caro,[13] in which the carbide was heated to a temperature of 800°-1000° and a current of nitrogen passed over it. It had already been shown by Moissan [29] that pure calcium carbide did not fix nitrogen below 1,200°, but it was found that the commercial carbides absorbed nitrogen at somewhat lower temperatures, and that this was due to a kind of catalytic action exerted by small amounts of metallic chlorides which were present. In the actual technical process, therefore, a quantity of calcium chloride (for example, up to 10 per cent. of the carbide in process) was added to the reaction mass, and under these conditions absorption of the nitrogen to the extent of 20 per cent. or more of the weight of carbide proceeds at about 800°. The reaction involved is as follows:—

$$CaC_2 + N_2 = CaCN_2 + C.$$

At higher temperatures, for example 1,200° and above, direct addition of nitrogen with formation of calcium cyanide, $Ca(CN)_2$, also takes place in appreciable

amount, and the function of the metallic chloride catalyst employed in the Frank-Caro process is thus not only to lower the temperature of reaction, but simultaneously to avoid producing the undesired cyanide.

The present production of cyanamide is probably in the neighbourhood of 400,000 tons, corresponding to about 100,000 tons of fixed nitrogen per annum. In one form of the process, the crushed carbide is heated in an electric furnace consisting of carbon rods passing down the centre of a number of iron drums lined with refractory bricks, whilst a current of nitrogen is passed through the series. The reaction is exothermic and proceeds after initiation by its own heat; the temperature is not allowed to exceed 1,000°–1,100°. About 20 per cent. of nitrogen is absorbed in the course of some twenty-eight hours, after which the drums are cooled and the product removed, pulverised, washed with water, and used mainly as a fertiliser under the name Nitrolim. Alternative methods are slowly to pass a series of trucks containing carbide through gas-heated airtight tunnel-ovens in which an atmosphere of nitrogen is maintained, or to pass a mixture of powdered carbide with calcium chloride or fluoride down a vertical furnace, fitted with alternating shelves which are heated electrically.

Whilst the main use of cyanamide is directly as a fertiliser it serves other purposes, one of which is its conversion into urea by careful treatment in concentrated aqueous solution with small amounts of sulphuric acid at about 70°–80°. More intensive action of water or steam converts the material entirely into ammonia and calcium carbonate, and the process is not one which lends itself too readily to high yields of urea. Consequently, although a certain amount of urea is technically produced from cyanamide as a fine chemical, the cost of production by this method may not permit urea to be marketed at the low price demanded by the fertiliser industry.

Urea from ammonia and carbon dioxide.—Within the last few years the possibility has been carefully investigated of employing the following reactions on a technical scale, and it would appear that successful processes for the production of urea from ammonia and carbon dioxide are now in being :—

$$(NH_4)_2CO_3 \longrightarrow H_2O + NH_2COO.NH_4$$
$$\longrightarrow NH_2CONH_2 + H_2O.$$

Theoretical data on the equilibria involved in these changes have been published by Matignon and Fréjacques [32] (1920–1922), and several descriptions have been given in the patent literature and elsewhere of means by which this reaction can be carried out on a large scale.

Thus the Badische Anilin und Soda Fabrik [33] describes a process in which two volumes of ammonia and one volume of carbon dioxide are heated for two hours under a pressure of 50–100 atmospheres and at a temperature of 135°–150°. Under these conditions a state of equilibrium is reached in the interaction

$$2NH_3 + CO_2 \rightleftarrows CO(NH_2)_2 + H_2O$$

in which about 40 per cent. of urea is present. The liquid product is either slowly released into a distilling column, when unchanged ammonium carbamate is decomposed into ammonia and carbon dioxide ; or the latter may be removed by cooling the charge in the autoclave to 60°–100° and reducing the pressure, when the same result is obtained. The recovered gases are compressed again and used in the production of further quantities of urea. The concentrated solution of urea leaving the still is further evaporated in vacuum concentrators and, according to a recent Badische patent, is obtained as a highly concentrated solution, which may be distributed into a chamber in the form of a moderately coarse spray ; the drops then solidify in sandy grains which are suitable for use as a fertiliser.

A Norwegian process [34] for producing urea consists in passing carbon dioxide at 130°–140° over ammonia compounds mixed with salts such as ammonium chloride or calcium chloride, when conversion to urea takes place, and the cooled product, after pulverisation, may be used directly as a fertiliser.

It will be noticed that the condensation of ammonia and carbon dioxide to urea, at all events by the Badische process, does not involve the employment of catalysts, but it is appropriate to refer to the method here since it forms one of the important outlets for synthetic ammonia produced by the catalytic process, whilst, in practice, the carbon dioxide used would generally be obtained from the operation of the catalytic water-gas hydrogen process carried on in conjunction with ammonia synthesis.

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CHAPTER IV

THE INDUSTRIAL CONVERSION OF AMMONIA INTO NITRIC ACID

THE catalytic production of nitric acid has been developed concurrently with the commercial synthesis of ammonia. Just as synthetic ammonia has relegated by-product sulphate and other forms of ammonia to a position of relatively minor importance, so also the production of nitric acid from Chile nitrate and sulphuric acid has been to some extent, and no doubt eventually will be completely, superseded by the technical oxidation of ammonia to nitric acid. It has been known for many years that ammonia can be directly oxidised in either of the following ways :—

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$
$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

Obviously if the oxidation can be controlled so that only the second of these processes comes into operation, nitric acid can be produced by the well-known further oxidation of nitric oxide, namely :—

$$2NO + O_2 = 2NO_2$$
$$\left\{\begin{array}{l} 2NO_2 + H_2O = HNO_3 + HNO_2 \\ 3HNO_2 = HNO_3 + H_2O + 2NO \end{array}\right.$$
or
$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The possibility of converting ammonia into nitric acid by passage of a mixture of the gas with air over heated spongy platinum was observed by Kuhlmann [5] in 1839, but no attempt was made to develop the process industrially until early in the present century, when Ostwald,[6] Frank and Caro,[7] and others worked out the technical conditions for an efficient process.

The Badische Company became interested in the matter from about 1910 onwards, when they were concerned with the development of synthetic ammonia

in Germany, whilst contributions were also made by F. Bayer & Co., and other German firms, all of whom are now constituents of the Interessengemeinschaft. In England the problem was systematically studied during the war period by the Ministry of Munitions, and a number of plants came into operation ; subsequently the process was taken up by independent firms, notably the United Alkali Company, and Synthetic Ammonia and Nitrates, Ltd. Considerable attention has also been paid in the United States of America to the catalytic oxidation of ammonia, both by the United States Government chemists and by several of the large industrial corporations.

Two distinct forms of catalyst have been proposed for the process, namely (i.) metallic gauze made of platinum or a similar metal, or (ii.) mixtures of metallic oxides, generally comprising a large proportion of ferric oxide with a smaller amount of certain other oxides such as, for example, that of bismuth. The latter type of catalyst has attracted attention, of course, in view of the somewhat heavy primary cost of installing platinum catalysts.

(To complete the story of present-day alternative propositions for the manufacture of nitric acid, mention may be made here of Häusser's explosion process,[4] whereby nitrogen and oxygen are caused to interact in an exploding mixture of a combustible gas and air. This process (which, of course, is not catalytic) is carried out in explosion bombs of about 300 litres capacity at an initial pressure of about 5–6 atmospheres. The bombs operate somewhat on the principle of the ordinary internal combustion motor engine with the usual Bosch ignition ; they are charged with a mixture of coke-oven gas and air, and after explosion the pressure rises to about 25 atmospheres. There are some forty-five ignitions per minute, and the exhaust gases, after release, are cooled to about 250°, and then in aluminium coolers to atmospheric temperature, after which the gases pass to an absorption

system and nitric acid is recovered and concentrated. It is claimed that this process should be cheaper than the alternative catalytic process now being described, but so far technical practice appears to favour the ammonia oxidation method.)

Theoretical Aspects of the Catalytic Oxidation of Ammonia to Nitric Acid.

Thermodynamical considerations and practical experience agree in showing that at practically any temperature the oxidation of ammonia is complete, so that quantitative yields should always be obtained, unless side reactions enter into the question. In point of fact, the reaction

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

which is primarily the result of dissociation of nitric oxide

$$2NO \rightleftharpoons N_2 + O_2$$

tends to take place if nitric oxide remains in contact with the catalyst unduly long. On the other hand, at very high rates of flow, there is difficulty in securing contact of the whole of the ammonia with the catalyst, so that some may escape oxidation ; this leads to a double loss, since the unchanged gas interacts with nitrous acid formed in a later stage of the process as follows :—

$$NH_3 + HNO_2 = N_2 + 2H_2O.$$

The condition necessary for a successful technical process is, therefore, mainly that oxidation of ammonia to nitric oxide should take place with maximum possible rapidity, all ammonia being completely oxidised, and none of the nitric oxide being further resolved into elementary nitrogen. In practice, using a platinum catalyst, a maximum efficiency of 95–97 per cent. can be obtained on a large scale, and the average efficiency of a modern plant is of the order of 92 per cent. conversion of ammonia to nitric oxide. Platinum catalysts are mainly used and are active

from 550° upwards, the action being rapid at about 700°–800°, when the time of contact of gas with platinum is less than 0.001 seconds. The cheaper forms of non-platinum catalysts are active at about the same temperature, but the oxidation is somewhat slower, and a contact time of from 0.01 to 0.03 seconds is usually necessary.

With increasing temperature, the reaction proceeds still more rapidly, but formation of elemental nitrogen tends to increase. The temperatures referred to are really the average temperatures of the gas mixture near the catalyst surface, and the actual working temperature of the platinum gauze itself is usually about 1,000°–1,025°. Owing to the strongly exothermal nature of the action

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 214{,}200 \text{ cal.},$$

the process can readily be made self-heating after an oxidation plant has once been started up.

The Platinum Catalyst Oxidation Process.

Platinum is employed in the form of very fine gauze, usually 80 mesh to the inch gauge made of wire 0.065 mm. thick. When a new gauze is put into operation it is somewhat slow in action, but the activity gradually increases until a maximum is reached. At this stage it is seen that the gauze, originally smooth and bright, has become dull and grey in appearance, and if examined under the microscope, it is found that the whole surface is pitted and roughened in an extraordinary manner; this, of course, is an excellent illustration of the fact that the interacting gases come into direct combination with the catalyst during change.

The mode in which the catalyst is exposed to the gases varies somewhat. In Ostwald's original process [6] the converter consists of an internal nickel tube about 8 ft. long and 2 in. in diameter, surrounded by an outer tube of enamelled iron. The catalyst consists of a roll of crumpled platinum foil (about

50 gm.) mounted in the top of the nickel tube ; the mixed gases enter the outer tube at the bottom, travel to the top and pass over the catalyst down the nickel tube, and serve to heat up the gases approaching the catalyst as they pass away to the exit. In the Frank-Caro process [7] the catalyst consists of a single rectangular layer of platinum gauze, 40 cm. by 60 cm., supported in an aluminium frame, between a lower aluminium vessel and an upper conical aluminium vent. Reference may also be made to the Kaiser apparatus,[8] in which the catalyst consists of several layers of platinum gauze placed close together across a tube of about 10 cm. diameter ; in this process the air is pre-heated separately to about 300°, and only mixed with ammonia immediately before reaching the platinum gauze.

These earlier processes have been more or less standardised in various recent plants, and a brief description may be given of German, British and American practice.

Details have been given by Partington [1] of the ammonia oxidation plant of the Höchst Farbwerke of the I.G. The catalyst consists of from 2–4 circular platinum gauzes of the usual mesh, 20 in. in diameter, supported on grids of stout platinum wire in a cylindrical cast-iron converter, fitted with conical ends. The ammonia-air mixture containing one part of ammonia to seven of air is filtered through linen cloth and passed direct to the converters, each of which has an output of 1·5 tons of nitric acid per day. The gas from the battery of 224 converters passes to four rows of eight brick absorption towers packed with stoneware rings, each of which is 41 ft. high and 21 ft. diameter. The sources of the ammonia are synthetic cyanamide and coal-gas liquor. The oxidation efficiency is 89 per cent., and the overall efficiency (including absorption and concentration of nitric acid) is 84 per cent.

A good example of British practice is the ammonia

oxidation plant of the United Alkali Company, described by Imison and Russell.[3] In this plant again a single layer of platinum gauze, 6 in. by 4 in. in size, is placed across a conical-shaped horizontal iron converter tube, the gauze being thus vertical. The converter is coupled to a tubular heat interchanger constructed of enamelled iron, or iron painted with a mixture of sodium silicate and barium sulphate. The ammonia-air mixture (one of ammonia to 7–9 of air) passes through the external part of the interchanger on its way to the platinum gauze, and its temperature is raised to about 300° by the heat of the oxidised gases passing through the internal tubes. The effect of pre-heating the gas mixture is to increase the efficiency of conversion to about 93 per cent. The main object of the United Alkali plants was to supply oxides of nitrogen for use in the chamber process of sulphuric acid manufacture ; the method has proved exceptionally serviceable for this purpose, as it has been found to be far cheaper than the old nitre pots, both in costs of material employed and in the labour and supervision required. At the same time, increasing amounts of nitric acid are being produced in Britain by this and other plants, the oxides of nitrogen being condensed and the acid concentrated as described below.

Recent description of American ammonia oxidation plants by Parsons [2] shows that the oxidation unit favoured is similar in general type to the British converter just described, but circular gauze cylinders are preferred to the flat gauze type, in that they are better adapted to large units and that it is easier to secure contact of all the ammonia with the gauze. The largest circular units in operation have a capacity for five tons of nitric acid per day.

The main points of difference in the present-day converters having been indicated, a more general description of the various phases of the process may now be given.

Sources of Ammonia.—The only point which requires

consideration as regards the origin of the ammonia is that of catalyst poisons. Phosphine, acetylene, sulphuretted hydrogen and silicon hydride may be present in traces in coal-gas ammonia or ammonia produced from cyanamide, and all these are toxic to a platinum catalyst. Since the cost of installation of the platinum gauze is an appreciable factor in the cost of the plant, it is necessary to make this, as far as possible, a capital charge, *i.e.*, the gauze must have a very long life and all catalyst poisons must be carefully removed. If synthetic ammonia from nitrogen and hydrogen is employed, catalyst poisons will probably be entirely absent. The other types of ammonia are best purified by scrubbing through strong caustic soda solution followed by passage over heated charcoal.

Another source of impurity which, according to Imison and Russell,[3] is more serious in its effects than that of the gaseous compounds referred to, is the presence of iron oxide or other dust in the gas mixture, which settles on the catalyst gauze and impedes contact between the active surface and the interacting gases. Precautions are, therefore, always taken to filter the incoming ammonia-air mixture through layers of linen cloth and/or layers of fine mesh metallic gauze.

In general, ammonia liquor containing from 20–27 per cent. NH_3 from any of the three sources mentioned is the starting material. This is fed down a fractionating column at the base of which a current of steam and air is admitted; the amount of air is so regulated as to give the desired proportion of ammonia and oxygen in the gas escaping from the top of the column. It is found that the presence of a little moisture in the gas mixture is beneficial rather than otherwise as regards the efficiency of the conversion. The gas mixture is then purified as indicated above, and passes on to the converters or heat-exchangers.

The ammonia-air mixture producing plant should

work, as far as possible, uniformly and almost automatically, delivering the mixture at a constant rate and constant in composition. After filtration from dust, the gas mixture should preferably only be exposed to aluminium, stoneware or enamelled (painted) iron plant in order to avoid picking up small particles of toxic metal oxides.

Practically all modern plants employ efficient heat-exchange systems between the oxidised gases and the air-ammonia mixture. As stated, Imison and Russell pre-heat the gas to about 300°, but other workers state that greater output (higher rate of flow of gas mixture) for a given efficiency can be obtained by pre-heating the gases to between 460° and 500°. It is probable that, so long as none of the gases are exposed to local temperatures greatly exceeding 1,000°, little falling off in efficiency of conversion takes place.

The cooled oxidised gases emerging from the heat-exchanger are dealt with in water or other absorption plants of the types about to be described.

Use of base-metal catalysts.—Brief reference must be made to the use of mixed-oxide catalysts in place of platinum, a technique which has been developed to some extent in certain of the German factories, although it is probable that under normal conditions platinum is preferred for various reasons to these cheaper forms of catalyst. In 1871, Tessié du Motay [9] patented a process for oxidising an ammonia-air mixture at 300°–500° by passage over chromates, manganates or other similar salts. Modern developments of this idea in the hands of the German chemical companies [10] have taken the form of mixed-oxide catalysts, for example, mixed oxides of iron and bismuth, iron and copper, iron and cerium, iron and tungsten, or iron and lead.

Little definite information is available as to the actual composition of the mixtures proposed, but apparently an iron-bismuth oxide catalyst employed technically in Germany consisted of about 95 per cent. iron oxide with about 3 per cent. of bismuth oxide. A Badische

patent describes catalysts consisting of copper oxide admixed with smaller amounts of lead peroxide or manganese dioxide, which are capable of oxidising a 7 per cent. ammonia-air mixture with a yield of 90 per cent. of oxides of nitrogen. Scott [11] states that the best non-platinum catalyst consists of a mixture of 97 per cent. of cobalt oxide with 3 per cent. of bismuth oxide, Bi_2O_3. These catalysts are employed in the form of a loose granular powder, and are active at about the same temperature as the platinum gauze catalyst, but operate considerably more slowly. It would also seem probable that the life of such catalysts would not be indefinitely prolonged as in the case of platinum gauze. The compactness and ease of operation of a platinum gauze catalyst unit are so marked that these features alone render the wide application of cheaper oxides unlikely, other than in exceptional circumstances.

Absorption of Nitric Oxide to Produce Nitric Acid.

In the case of ammonia oxidation the actual catalytic process is simpler and far more compact than the subsequent processes of converting the nitric oxide into nitric acid of commercial quality. This follows as a consequence of the two actions previously mentioned (p. 120), which are involved in the oxidation of nitric oxide to nitric acid :—

$$2NO + O_2 = 2NO_2$$
$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The oxidation of nitric oxide to nitrogen peroxide proceeds comparatively slowly ; for example, if the nitric oxide-air mixture contains 10 per cent. of the former gas, at least $2\frac{1}{2}$ minutes is required for complete oxidation. A further complication is that in the conversion of nitrogen peroxide to nitric acid, one-third of the nitrogen is again liberated in the form of nitric oxide, which requires re-oxidation. We thus have an exceedingly fast ammonia oxidation process followed by relatively slow conversion of nitric oxide to nitric acid, and this is reflected in the technical plant by the

necessary provision of absorption towers of very large size compared with the space occupied by the actual ammonia oxidation plant.

Further, in consequence of the slow and repeated oxidation which is necessary in the absorption towers, the concentration of the nitric acid finally produced tends to be on the low side and, as a rule, the strength of the acid from the towers is only about 50–55 per cent. HNO_3. Again, owing to the vapour pressure of mixtures of nitric acid and water, which are characterised by a minimum vapour pressure for an acid containing about 70 per cent. HNO_3, the final composition of the residue when dilute nitric acid is distilled is never more than 70 per cent. HNO_3 (b.p. 121°). Consequently nitric acid cannot be concentrated by straight distillation, and other methods have to be resorted to in order to produce 100 per cent. nitric acid.

The general principles adopted in the absorption of nitric oxide, or rather its oxidation to nitric acid, are to cool the oxidised gases from the ammonia oxidation converter in a gas-cooler, which may be constructed of aluminium or of chrome steel. In the course of cooling, the water produced in the original oxidation is separated to a large extent, and utilised later in the absorption towers. Efficient removal of the water present at this stage increases the concentration of nitric oxide and oxygen in the reacting gases, and favours the oxidation process. Some difference of opinion appears to exist with reference to the temperature at which the oxidation to nitrogen peroxide occurs most rapidly, but in modern practice this part of the process is generally conducted at as low a temperature as possible, that is to say, practically at atmospheric temperature.

The cooled gases are usually mixed with a further quantity of air (known as " secondary air "), before passage to the absorption towers, which may be constructed of stoneware, acid-resisting bricks or acid-resisting metal. A special chrome steel containing 17 per cent. of chromium is at present coming into

considerable favour; this is entirely unaffected by nitric acid and also by atmospheric conditions. In view of the latter fact, and of its good conductivity for heat as compared with stoneware, etc., this is a useful advantage in that the absorption towers may be exposed direct to the external atmosphere so that maximum removal of the heat evolved in the oxidation of the nitric oxide is secured.

The first absorption tower is usually empty, and serves simply as a chamber in which the initial oxidation of nitric oxide to nitrogen peroxide is effected as far as possible. The remaining towers are filled with packing material (which may consist of coke, Guttmann balls or Raschig rings, etc.); the packing employed should expose a maximum of surface area per volume of material and at the same time should be such that when packed in the tower it leaves as large a free gas-space present as possible, so that the slow oxidation process may have every opportunity to complete itself in the gaseous phase.

In the towers a slow current of water trickles down over the surface of the packing, and meets the ascending nitrous gases, when the reactions previously referred to proceed, with regeneration of successively smaller concentrations of nitric oxide, which continues to be oxidised by the air present until at the exit from the last tower the process is practically complete. If the amount of water employed is controlled so that the average concentration of the nitric acid produced does not fall below 50 per cent., it is not possible to obtain complete absorption of nitrogen peroxide, and the final exit gases must be dealt with in some other way; usually this consists of final scrubbing through a tower containing dilute caustic soda solution, the final gases thus being converted into sodium nitrate.

It may be useful very briefly to illustrate the above by reference to various types of absorption plant.

For example, at the Höchst works (p. 124), the gases containing nitric oxide and steam pass through eight

cast-iron mains, 18 in. in diameter, to four rows of eight absorption towers each, each row being provided with twelve intensive coolers of special design, 5 ft. high and 2 ft. 6 in. in diameter, constructed in aluminium. The gas is passed through the coolers at high speed, and practically only water condenses, the condensate being used in the fifth absorption tower. The gases leaving the coolers at 30° are mixed with "secondary air" and passed through stoneware mains to the sets of absorption towers. The towers are constructed of brickwork, and are 41 ft. high and 21 ft. in diameter, packed with stoneware rings, leaving a total internal volume of about 35,000 cubic feet of gas space. This is distinctly on the low side, but at the Höchst factory 25 per cent. of the nitric oxide made is finally converted into nitrate of soda. The first towers are fed with water in order to produce nitric acid, which is obtained at an average concentration of 50 per cent., whilst the last two towers of the series are fed with saturated sodium carbonate solution in order to produce sodium nitrate. The efficiency of the whole absorption plant is said to be 97 per cent. The 50 per cent. tower acid is concentrated by mixing with sulphuric acid and de-nitrating as described below.

Imison and Russell's description[3] of the United Alkali Co. plant indicates that liquid nitric acid was produced by passage of the oxidised gases through stoneware towers, each 3 ft. in diameter by 16½ ft. high, the first of which was empty, the following three being packed with rings and fed with water, and the last two similarly packed, but fed with soda solution. This plant served to deal with the oxidised gases from a single converter with 6 in. by 4 in. gauze, and would produce about one ton of 100 per cent. nitric acid per week, the acid being actually obtained at about 50 per cent. HNO_3, whilst 5–6 per cent. of the total was in the form of sodium nitrate. The concentration of the 50 per cent. nitric acid was effected by heating with sulphuric acid in a de-nitrating tower of the usual type.

A recent description [2] of American practice indicates that the absorption plant is constructed throughout of chrome steel, and comprises gas-coolers followed by a series of absorption towers, comparable in proportions with those used in Germany. Fifty to 57 per cent. nitric acid is obtained from the water-absorption towers, and in the final tower of the system, constructed of ordinary steel, the 2–3 per cent. of the total nitric gases which have escaped absorption as dilute nitric acid are converted into sodium nitrate by means of sodium carbonate solution. The absorption efficiency is of the order of 95–96 per cent.

Production of Concentrated Nitric Acid.

Practically the only method at present employed for concentration of the 50 per cent. acid produced in the absorption towers consists in mixing, say, seven parts of the dilute acid with one part of concentrated sulphuric acid and distilling the mixture from a cast-iron pot-still. The process may be made continuous by employment of a de-nitrating tower, which is practically an acid-resisting fractionating column, filled with acid-resisting packing and fed with a constant stream of concentrated sulphuric acid. The 50 per cent. dilute nitric acid is vaporised into the base of the tower and passes up through the descending sulphuric acid. The result is that the water is transferred from the nitric acid to the sulphuric acid, and nitric acid of 96–97 per cent. strength distils away from the head of the tower and is condensed in aluminium or chrome steel pipes and, if necessary, finally passed down a small stoneware tower, where it meets a current of compressed air, which removes any residual oxides of nitrogen.

The diluted sulphuric acid leaving the base of the de-nitrator is re-concentrated (for example, in a Gaillard tower) and used again.

Other suggestions have been made in order to avoid the somewhat elaborate de-nitration process. For example, Meister, Lucius and Brüning [12] have taken

out patents for enriching 60 per cent. nitric acid obtained in absorption towers with nitrogen peroxide, and submitting the solution obtained to the action of oxygen, with the result that the action

$$2NO_2 + H_2O = HNO_3 + HNO_2,$$

followed by oxidation of most of the nitrous acid to nitric acid takes place, and consequently the concentration of the acid is considerably increased. A recent patent by Cederberg [13] indicates that, if no water other than that formed in the original oxidation of ammonia is present, it is possible to effect absorption of the nitric oxide in such a way that a 70 per cent. acid is produced.

It seems, however, that the sulphuric acid denitration process is, on the whole, the most economical for effecting production of concentrated nitric acid from ammonia. If it were possible to obtain 100 per cent. nitric acid by simple distillation the synthetic nitric acid process would be much simpler and exceptionally efficient. It is, of course, possible to produce larger proportions of the acid from the oxidised gases in the form of sodium nitrate or, for example, of calcium nitrate, and where metallic nitrates are required as such for fertilisers, etc., this is simple and convenient. So far as the production of the concentrated acid is concerned, however, it is obviously uneconomic to have recourse to the intermediate production of sodium nitrate, which would again involve distillation with sulphuric acid and production of the practically waste nitre cake (acid sulphate of soda) as by-product.

Fauser [14] has lately described a process for the oxidation of ammonia under pressure (5 atmospheres), which has been successfully carried out on a technical scale (10 tons of nitric acid per day). Although the rate of oxidation is but little accelerated, great economy is effected in ground-space and in steam (heat), whilst the important feature is that acid containing 74–75 per cent. HNO_3 can be directly produced. The

amount of sulphuric acid required to concentrate nitric acid of this strength to pure nitric acid is only one-quarter of that necessary for producing the same weight of concentrated acid from 50 per cent. nitric acid.

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Acid Concentration

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CHAPTER V

THE SULPHURIC ACID INDUSTRY

SULPHURIC acid has been manufactured for nearly 200 years by one or other of two alternative catalytic processes. The older process, known as the Chamber Process, goes back to somewhat before 1750, and is extremely interesting from a theoretical standpoint, because it is one of the very few cases in which catalytic action proceeds (to a certain extent, at all events) in a homogeneous gaseous system ; the earliest explanation of the processes operating in the sulphuric acid chambers was given by Sir Humphrey Davy about 1812. The greater part of the world's production of sulphuric acid is still carried on by the chamber process, but during the past fifty years the Contact Process, which consists of interaction of sulphur dioxide and atmospheric oxygen at the surface of a solid catalyst, has developed considerably, especially in conjunction with the manufacture of fuming sulphuric acid, technically known as oleum.

For the sake of compactness, both processes of sulphuric acid manufacture will be considered in the present chapter, although only the modern contact process belongs strictly to the heterogeneous type of catalytic action with which we are concerned in the present section of this book. For the latter reason, and also in order to bring the catalytic oxidation of sulphur dioxide more closely into relationship with the oxidation of ammonia described in the previous chapter, the contact process will be dealt with before describing the older chamber process ; the latter, although it is a case of homogeneous catalysis in either a gaseous or a liquid system, forms the subject of the concluding part of the present chapter.

Before proceeding to describe either process, how-

ever, it is well to glance at the general conditions of the sulphuric acid industry at the present day, and also to consider the various sources from which sulphur dioxide is at present obtained for use in either process.

A statesman of the Victorian era is reported to have said : " Show me the state of the sulphuric acid industry, and I will tell you the state of trade in England." At the period in question, sulphuric acid was necessary for the manufacture of alkali by the Leblanc method, for the production of phosphate manures from bone for agriculture, for the extraction of various metals, and for very many other purposes ; so that to a large extent, sulphuric acid was indeed the backbone of the chemical industries, and therefore indirectly of an important part of the manufacturing trades of the country. It is pleasant to reflect that even in the middle of last century a politician was to be detected who seems to have realised that " Chemicals form the Foundation of the World's Industries."

At the present time matters have altered considerably and probably permanently, for sulphuric acid is being displaced in several industries from its former position as an integral agent in the manufacture of various compounds. Thus, phosphoric acid is beginning to be produced from natural phosphates by volatilisation methods, leading to the production of phosphatic nitrogen fertilisers in which calcium superphosphate (made by the action of sulphuric acid) is absent. Again, the Leblanc soda ash process is on the verge of extinction, at all events in this country, and alkali is now made either by the ammonia-soda method or electrolytically. Both by-product ammonium sulphate and nitric acid from Chile nitrate involved the use of sulphuric acid ; the new methods of obtaining fixed nitrogen are tending more and more to dispense with the use of sulphuric acid altogether. Although at an early stage synthetic ammonia was absorbed in solutions of free sulphuric

acid, present practice almost invariably favours the double decomposition of ammonium carbonate with a suspension of natural calcium sulphate, and it is quite likely that the by-product ammonia producers will follow the lead of their synthetic competitors and adopt a similar system for conversion of the coal-gas ammonia into sulphate. Similarly, the catalytic method of producing nitric acid requires sulphuric acid only during the concentration of the nitric acid solutions produced, and the concentration process requires make-up sulphuric acid only to replace mechanical losses.

On the other hand, although these important industries have tended to eliminate sulphuric acid to such a large extent, it must not be forgotten that many industries, such as the manufacture of organic chemicals, dyestuff intermediates, artificial silk, are expanding steadily, and in some cases rapidly, and that sulphuric acid must always be an important reagent in manufacturing processes of these and other kinds. Therefore, although it is quite possible that the production of sulphuric acid has reached something approaching its maximum, it is not likely that the demand for this acid will fall off to a very great extent under normal conditions of trade.

Some figures illustrating the production of sulphuric acid in recent years may now be given :—

Relative Production of Chief Manufacturing Countries, 1913.

	Tons (100 per cent. H_2SO_4).
United States . . .	2,200,000
Germany	1,600,000
Great Britain . . .	1,150,000
France	875,000
Italy	419,000

Production in Great Britain, 1915–1924.

	Tons (100 per cent. H_2SO_4).
1915	1,083,000
1916	1,320,000
1917	1,382,000
1918	1,131,000
1921	561,000
1922	818,000
1923	854,000
1924	890,000

In England the bulk of the acid produced is still made by the chamber process, although in 1917 over 220,000 tons of contact process sulphuric acid were made in this country. The present output of contact sulphuric acid in England is apparently about 50,000 tons per annum, or less than 10 per cent. of the total output. The same state of affairs holds in other countries, even in Germany, where the relative proportions are probably about 30–40 per cent. contact acid and 60–70 per cent. chamber acid.

Technical Sources of Sulphur Dioxide.

The chief sources of sulphur dioxide, which is the raw material for sulphuric acid, include iron pyrites, elemental sulphur, spent iron oxide, natural calcium sulphate (gypsum or anhydrite), other metallic sulphides such as zinc blende or copper ores, and spent alkali waste.

Until comparatively recent times, the main source of the gas was iron pyrites, especially Spanish pyrites, which usually contains about 3–4 per cent. of copper as sulphide. The pyrites is heated in a current of air at about 400°–500° in furnaces or "burners," which are usually mechanically operated. The older reverberatory type of burner [1] has long been replaced by rotary furnaces of the MacDougall, Herreshoff or

other types,[2] consisting of a vertical cylinder with fixed horizontal trays, furnished with a central shaft carrying rotary scrapers. Inclined rotary kilns somewhat similar to a cement kiln are also used in some installations. The saving of labour accomplished by the use of mechanical burners is to some extent mitigated by the production of considerable amounts of flue dust in the exit gases, although this is minimised by employing only natural draught for the gases in the ovens. It is necessary, however, to pass the pyrites-gases through large chambers fitted with baffles which act as dust separators, in order to produce sufficiently clean gas for the operation of the chamber process. Even this provision is not enough to cleanse the gases adequately for use in the contact process, for they still contain minute suspended particles of ferric oxide, and especially of arsenious oxide, As_4O_6, which are strongly toxic to the platinum catalysts employed. Further purification (although still not sufficient for purposes of the contact process) is effected in modern pyrites-burning plants by the installation of a Cottrell electrostatic dust precipitation plant, through which the flue gases are led. Recently a new type of pyrites-burner has been introduced, known as the Bracq-Laurent burner[3, 4] which consists of a sloping hearth constructed of refractory material carrying a layer of pyrites, which is raked forward by moving arms which describe elliptical movements owing to the rotation of a central shaft to which they are fitted. The shaft is rotated alternately in either direction, and the result of the motion is to produce in the pyrites a series of trenches which are successively swept forwards in a downward direction. The result of this method of raking the pyrites is to tend to keep it at the surface of the hearth and to minimise dust formation. In fact, it is stated that the operation of this burner at several Continental works has justified the designers' claims that its employment dispenses with the necessity for any dust

separator, so far as the production of chamber acid is concerned.

In cases where spent iron oxide from gas works is the source of the sulphur dioxide, the burners employed are somewhat similar to those used for pyrites.

It should be noted that the oxidation of iron sulphide is a burning rather than a roasting process, that is, once the oven has been started by the use of a few spadefuls of red-hot coke, oxidation of the pyrites proceeds exothermally and continuously.

An increasingly important source of sulphur dioxide is elemental sulphur, which is now obtained largely from the West Indies, Texas and other parts of the southern United States from subterranean deposits of natural sulphur. This is usually extracted by the Frasch process, in which a shaft is drilled into the deposit and fitted with an internal aluminium pipe. Steam at about 100 lb. pressure is passed down the external shaft until a sufficient quantity of the sulphur deposit is melted; the steam is then replaced by compressed air, which forces the fused sulphur and hot water up the central tube, at the outlet of which the sulphur is collected in large tanks and obtained in a condition of over 99 per cent. purity.

Native sulphur of this kind is usually burnt in a stationary furnace on layers of iron trays, the furnace being supplied at the base with a current of air; rotary furnaces are also employed. The design of an efficient sulphur burner is more difficult than that of a pyrites burner because temperature control is much more important; it is necessary to avoid overheating, since, in addition to obtaining too rapid fusion of the sulphur it is easily possible to lose sulphur by distillation and sublimation.

Sulphur obtained from alkali waste by the Chance process (this section, Chapter VIII, p. 198) was formerly used to some extent in sulphuric acid manufacture, and was burnt in ovens of design similar to those now used for native sulphur.

An appreciable proportion of sulphur dioxide is also obtained, especially in America, Germany and Belgium, from the roasting of zinc blende and nickel-copper sulphide ore residues. The temperature necessary to convert this class of sulphides into oxides is considerably higher than in the case of iron pyrites, namely, about 800°–900°. The operation is carried out in a closed or muffle furnace, which consists, in the Hasenclever type,[5] of a number of horizontal furnaces completely enclosed in a series of horizontal flues for the heating gases. By means of another series of flues passing through the interior of the muffles, hot air is passed over the surface of the ore. The fuel consumption required in treating these ores is, of course, much greater than in the case of pyrites burning and amounts to about 15–20 per cent. of the weight of ore treated. The cost of this fuel is balanced, of course, by the higher value of the residual metals (zinc, copper, or nickel) which are subsequently extracted from the calcined ore.

Finally, processes have recently been developed in Germany [6] for the conversion of gypsum or anhydrite into sulphur dioxide and Portland cement, depending on the primary action

$$CaSO_4 + C = CaO + SO_2 + CO.$$

The operation is carried out in a rotary kiln in which the powdered mineral meets a current of pulverised fuel. In order to recover the lime in an economic form, the mineral calcium sulphate is first intimately mixed with clay and the mixture dried before entering the kiln. An oxidising atmosphere is maintained in the kilns, so that the carbon monoxide formed is converted to carbon dioxide during the process, and also formation of carbon oxysulphide or calcium sulphide is minimised. The cement produced is ground with blast-furnace slack and sold as blast-furnace cement, whilst the exit gases from the kiln contain 6–7 per cent. of sulphur dioxide, and are washed and passed through a

Cottrell electrical separator, when they are ready for use in the manufacture of sulphuric acid either by the chamber or the contact process.

A table may be given in conclusion to illustrate the general composition of gas mixtures produced by the above methods.

Name of Mineral.	Percentage Sulphur Dioxide.	Percentage Oxygen.	Percentage Nitrogen.
Pyrites. . .	7–8	6–11	81–87
Sulphur . .	10–11		
Blende. . .	9	8	83
Gypsum . .	6–7	6–10	83–88

For many purposes, such as for electrical accumulators, or for use in connection with edible products, such as invert sugar, fats, glycerine, etc., it is urgent that the sulphuric acid employed should be entirely free from arsenic. Whilst, as indicated later (p. 156), it is possible to remove traces of arsenic quite efficiently and fairly cheaply from the finished sulphuric acid, it is also of considerable advantage in such cases to employ raw material which is practically arsenic-free ; in other words, in the production of arsenic-free acid it is desirable to use sulphur dioxide prepared either from pure native sulphur or by the gypsum process.

The Contact Sulphuric Acid Process.

This method, which consists in passing a mixture of sulphur dioxide and oxygen over a catalyst which may be either composed of platinum or of oxides of iron and certain other metals, is obviously similar in general principles to the Kuhlmann process of oxidation of ammonia to nitric acid. Like the latter, the possibility of carrying out this reaction was known for many years before means were found to put it into technical practice. Sir Humphrey Davy, in 1812, suggested that spongy platinum might serve as a catalyst in the production of sulphur trioxide, and in 1831, a patent was

actually taken out by Phillips [7] for this process, but technically it was a failure, as the platinum invariably rapidly lost its power of effecting the oxidation. The method was allowed to lapse for nearly fifty years, until Squire and Messel,[8] in 1875, succeeded in maintaining the activity of the platinum on a commercial scale, by employing mixtures of sulphur dioxide and oxygen prepared in a special manner ; they either produced the mixture from concentrated sulphuric acid by passage over red-hot firebrick :—

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2,$$

or by burning specially purified sulphur in air. The gases were dried by means of sulphuric acid and then passed over finely-divided platinum and absorbed in strong sulphuric acid, thus producing the so-called fuming acid, $H_2S_2O_7$.

At the period in question the demand for fuming sulphuric acid (oleum) was growing considerably with the rapid expansion of the synthetic dyestuffs industry, where it was required in many processes of sulphonation and nitration. The only source of this acid prior to Squire and Messel's process was distillation of ferrous sulphate in a current of air by the old Nordhausen process :—

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$
$$2SO_2 + O_2 + Fe_2O_3 = Fe_2O_3 + 2SO_3$$

This explains why Squire and Messel's process, which, starting from sulphuric acid, at first sight seems to be uneconomic, became a profitable source of oleum, $H_2S_2O_7$, for many years.

Naturally, however, attempts continued to be made [9] to utilise the platinum oxidation process for the ordinary sulphur dioxide-air mixture produced, for example, from pyrites-burners, and the German dyestuff companies, especially the Badische Company and Meister, Lucius and Brüning, investigated the process both from the point of view of general physico-chemical considerations and also with reference to rapid

poisoning of the catalyst. This work led to the production of contact sulphuric acid on a technical scale in Germany towards the end of the nineteenth century.

It should again be pointed out, however, that although the contact process has reached a very high state of efficiency, the older chamber process is also highly efficient and economical in working, and still has the advantage over the contact process so far as production of ordinary commercial oil of vitriol is concerned. The chief technical value of the contact process lies in its utility as a source of oleum, which is used not only in sulphonation and nitration processes of the dyestuffs industry, but also in the nitration of cellulose for the production of explosives, celluloid, etc., and in the recovery of waste nitric acid from these and other nitration processes. The detailed study of the action

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

was mainly carried out by Knietsch[10] and his collaborators, who showed that higher percentages of sulphur trioxide in the equilibrium mixture would be realised the lower the temperature, that the temperature should preferably be maintained at or below 450°, and that the yield of sulphur dioxide is increased with increasing concentration of oxygen in the original gas mixture, subject to the restriction that undue dilution owing to the presence of atmospheric nitrogen again tends to reduce the yield. Maximum working yields are obtained when the oxygen is present in three times the theoretical amount demanded by the above equation, that is, two volumes of sulphur dioxide to three volumes of oxygen or fifteen volumes of air. Under the latter conditions 98 per cent. conversion to sulphur trioxide is obtained at 400°–450° as against 91 per cent. conversion employing the theoretical amounts of sulphur dioxide and air. Other physico-chemical data dealing with this reaction are to be found in the subsequent work of Bödlander,[11] Bodenstein[12] and their collaborators.

The second and more vital problem for the commercial success of the process, namely, the removal of impurities toxic to the catalyst, was also successfully solved. It has been indicated that Squire and Messel, realising that the source of the catalyst poisons lay in the pyrites gases, employed purer forms of sulphur dioxide-oxygen mixtures. Knietsch and Krauss[10] established definitely that the actual poison was the dust contained in the pyrites, mainly ferric oxide, which also contained appreciable traces of arsenic and selenium, both strongly poisonous to catalytic platinum. If these impurities were carefully removed by drastic scrubbing processes to such an extent that they exhibited no fog in a strong beam of light, the platinum was found to maintain its activity at a constant value almost indefinitely. The actual form of gas purification adopted on the large scale by the Badische Company consisted in injecting atomised steam into the gases from the pyrites-burners, followed by cooling to 100° in a lead condenser, and scrubbing in a series of towers with water, after which the gases were passed through a tower scrubber containing strong sulphuric acid.

It should be mentioned that in the course of Knietsch's comprehensive investigation of the process it was found that in addition to platinum distributed on various supports (for example, pumice, firebrick, asbestos), oxides of iron, chromium, vanadium and similar metals, including a number of the oxides of the rare earth metals, were also more or less efficient as oxidising catalysts. The catalysts of the oxide class, however, operate at considerably higher temperatures, namely, about 700° instead of 400°–450°, and under these conditions the percentage of sulphur trioxide in the equilibrium mixture is only of the order of about 60 per cent. The latter type of catalyst, in the form of ferric oxide, nevertheless has an advantage in that passage of pyrites-burner gases over a mass of burnt pyrites (that is, ferric oxide containing traces of other oxides) at about 700° has the double effect of removing

flue dust and fixing all arsenic and similar impurities, whilst at the same time about 60 per cent. conversion to sulphur trioxide is also achieved. This procedure is therefore utilised in what is known as the Mannheim contact process,[13] in which gas purification and considerable production of sulphur trioxide is secured simply by passage of the original gas mixture through ferric oxide, the conversion to sulphur trioxide being completed by subsequent passage over platinum catalyst. We proceed to describe the three main forms of the contact process at present generally used, namely, the Badische, Grillo and Mannheim processes.

The Badische Contact Process.—The Badische converter consists of a fairly large cylindrical iron vessel, in the interior of which a number of vertical iron tubes are set, somewhat in the form of a tubular condenser. The inner tubes are packed loosely with asbestos fibre on which 10 per cent. of platinum has been deposited, usually by impregnation with platinum chloride followed by reduction with an alkaline formaldehyde or formate solution.

The mixture of sulphur dioxide and air from the pyrites or other burners, containing as a rule about 7 per cent. sulphur dioxide and 10–11 per cent. oxygen, has been purified by intensive cooling and scrubbing as described above, and enters at the base of the external iron converter and passes upwards, where it is directed by an arrangement of baffle flues into the tops of the interior catalyst tubes, which are maintained at 400°–450°. The oxidised gases enter a common flue at the base of the catalyst tubes and pass away to a series of sulphuric-acid towers, in which the sulphur trioxide is absorbed so as to produce oleum, usually containing 60 per cent. sulphur trioxide.

The action $2SO_2 + O_2 = 2SO_3 + 21{,}700$ cals., is sufficiently exothermic to allow the process to proceed without external heat once it has been set going. It is important, in order to secure total conversion, to ensure that the temperature of the catalyst does not rise above

about 500°, and this is aided by a system whereby the entering gases are admitted not only at the base of the converter as described, but can also enter at one or more other points higher up the converter. Thus, by controlling the intake of the purified gas mixture, the temperature in the catalyst tubes can be closely regulated.

The Grillo Process.[14]—This is generally considered to be the most efficient form of the contact process. It is distinguished from the other processes by the employment of a special form of platinised magnesium sulphate as catalyst ; this is prepared by impregnating the ordinary hydrated sulphate, $MgSO_4 , 7H_2O$, with a solution of platinum chloride and placing the dried impregnated material on a number of superimposed iron trays set in a vertical converter, heated initially by flue gases and, subsequently, by a process of heat exchange somewhat similar to that used in the Badische converter. On heating the impregnated magnesium sulphate in a current of sulphur dioxide and air the anhydrous salt is produced in a somewhat voluminous bulky form, whilst at the same time the platinum salt is decomposed and the metal set free. The extensive surface thus produced causes this form of catalyst to be highly active with reference to the space occupied ; for example, it is possible to produce one ton of oleum per day from about 1·75 kg. of catalyst containing not more than 5 gm. of platinum.

The gases, before entering the converter, are purified in the same manner as in the Badische process, and the plant is so worked that a temperature of 400° or somewhat less is maintained in the converter ; the exit gases from the converter are absorbed in concentrated sulphuric acid as in the former case.

The Mannheim Process.[13]—This is designed on somewhat different lines from the two preceding processes, and was worked out by Clemm and Hasenbach at about the same time (1898) as the first Badische processes came into operation. As already stated,

the oxidation is conducted in two phases, in the first of which ferric oxide is employed both as a preliminary catalyst and also in order effectively to purify the crude pyrites-burner gases.

The installation is somewhat complicated, but consists essentially of a set of suitably designed pyrites-burners, the gases from which enter an oven in which burnt pyrites, which has already been used as a source of sulphur, is heated to 600°–700° on a revolving hearth. The gases from the burners pass upwards through the red-hot burnt pyrites, and some 50–60 per cent. of the sulphur dioxide is converted to trioxide, whilst the dust impurities, etc., are being removed. The exit gases are scrubbed through strong sulphuric acid, which removes the sulphur trioxide already formed, and are then passed through coke scrubbers to remove sulphuric-acid mist, and proceed to the platinum converter, which is maintained at about 450° and contains platinised asbestos.

It is difficult to say which of these processes is the most efficient in actual working; the compactness of the Grillo installation and the combined purification and partial conversion of the Mannheim process are points in favour of these, both of which were operated by the Ministry of Munitions in this country during the war. The general conclusion of the Ministry was that the Grillo process was on the whole the most efficient and economical under the conditions then obtaining.

The restriction of the contact process to the production of oleum seems at first sight to be unnecessary since, assuming that working costs permitted, it is evident that the ordinary concentrated acid or "monohydrate" H_2SO_4 should be produced by absorption of the sulphur trioxide in water instead of employing strong sulphuric acid. The technical objection to this procedure is that it is almost impossible to absorb the suspension of solid sulphur trioxide in the exit gases by means of water. The sulphur trioxide mist,

in spite of the strong mutual attraction between sulphur trioxide and water, is only very partially absorbed when the gases containing it are exposed to the action of water, even in an efficient scrubbing plant. As the older chamber process is equally economical to run and gives highly efficient conversion of sulphur dioxide to sulphuric acid, it is probable that the contact process will be restricted to the production of the fuming acid.

The Chamber Sulphuric Acid Process (a Case of Homogeneous Catalysis).

The operation of the chamber process is so thoroughly dealt with in numerous monographs, and is also so familiar to the most elementary student of chemistry, that its formal description may be replaced in the present book by consideration of (1) the catalytic actions which take place, and (2) the modern modifications introduced into the process with a view to economy of chamber space and efficient concentration of the Glover acid.

The process dates from about 1740, lead chambers being first introduced by Roebuck in 1746. It was not until about thirty years later that steam was supplied to the chambers in addition to the mixture of moist sulphur dioxide and nitrous gases from the pots. At the close of the 18th century, Clément and Désormes investigated the process and indicated the main reactions which took place, and in 1812 Davy put forward the view that the nitrogen oxides were concerned in the transformation of sulphur dioxide to trioxide, and suggested that the process could be summed up in the following way :—

(1) $2SO_2 + 3NO_2 + H_2O = 2SO_2\begin{<}{OH}{NO_2}\end{} + NO$

(2) $2NO + O_2 = 2NO_2$

(3) $4SO_2\begin{<}{OH}{NO_2}\end{} + O_2 + 2H_2O = 4H_2SO_4 + 4NO_2$

The vital parts of a chamber plant are the Glover tower, the chambers and the Gay-Lussac tower. The reactions referred to take place almost entirely in the chambers and (in the older types) to a considerable extent in the gaseous phase; but it seems probable that part of the oxidation always occurs in the liquid phase in aqueous solution either as mist or on the walls of the chambers. The main function of the Glover tower is to concentrate the relatively weak acid produced in the chambers, and at the same time to eliminate therefrom dissolved oxides of nitrogen; it is, therefore, worked on the counter-current system, chamber acid flowing down the tower and meeting a stream of air from the pyrites burners containing from 6–12 per cent. of sulphur dioxide together with a certain amount of oxides of nitrogen produced from nitre pots, or in modern plants by oxidation of ammonia. The hot gases concentrate the chamber acid from about 65 per cent. to 78 per cent. (commercial oil of vitriol), carry forward with them oxides of nitrogen dissolved in the chamber acid, and are simultaneously cooled to the working temperature of the chambers.

The Gay-Lussac tower, which, like the Glover tower, is packed with earthenware balls or hard coke, is connected with the gas exit of the chambers and fed with a slow stream of concentrated sulphuric acid. The result is that any oxides of nitrogen passing away with the nitrogen and other spent gases are absorbed with production of the so-called nitrous vitriol, the main component of which is nitro-sulphonic acid, $SO_2(OH)NO_2$. This tower is maintained at a temperature of about 30°–40°, a higher temperature leading to the decomposition of the nitro-sulphonic acid. The volume of the Gay-Lussac tower should be at least one per cent. of that of the chamber space, and frequently in modern works two Gay-Lussac towers are installed in series.

The Gay-Lussac tower is constructed of masonry

lined with sheet lead, and is usually 32–50 ft. high by 4–10 ft. wide. The Glover tower is similarly lined with very stout lead and fitted with an internal lining of acid-resisting bricks; acid-resisting stoneware is the usual packing employed in this tower, which is about 25–30 ft. high by about 6 ft. in diameter. In addition to the chamber acid, nitrous vitriol from the Gay-Lussac tower is also supplied at the head of the Glover tower, and the upper part of this tower is mainly concerned in de-nitrating the sulphuric acid according to the reaction

$$2HSNO_5 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

In modern plants this process accounts for as much as 25–30 per cent. of the total sulphuric acid make. At the same time the burner gases, as already stated, are cooled to the chamber temperature in the upper part of the Glover tower and also carry with them aqueous vapour, removed from the sulphuric acid, which forms part of that required for the chemical action proceeding in the chambers. The function of the lower part of the Glover tower is almost exclusively concentration of the sulphuric acid by means of the hot burner gases.

Coming now to the part of the plant in which the main catalytic action is carried out, namely, the chambers, and confining our attention in the first place to the old-fashioned type in which the necessary amount of water vapour was made up by injection of steam, the chambers were usually about 100–130 ft. long by 20–30 ft. diameter and 15–25 ft. high. Each unit was constructed of pure lead sheets supported on a wooden framework, and, as a rule, three, or sometimes four of them, were connected in series. The reactions proceeding in the chambers have formed the subject of many detailed investigations [15] since the original work by Davy and by Clément and Désormes, the most informative being that of Lunge and Naef, published between 1884 and 1890. In presence of insufficient moisture in the chambers,

a deposit of solid "chamber crystals" takes place, these consisting of Davy's nitro-sulphonic acid. Lunge and Naef carried out an exhaustive examination of the composition of the gases in each chamber, and found that after the first (in which the gases were colourless) the oxides of nitrogen present were coloured and consisted of equimolecular proportions of nitric oxide and nitrogen dioxide, which behaved as N_2O_3 :—

$$NO_2 + NO \rightleftharpoons N_2O_3.$$

They therefore modified Davy's conception of the chamber processes by assuming that the actual catalyst, so to speak, was N_2O_3 rather than alternately NO_2 and NO as in Davy's explanation :—

$$(1)\ 2SO_2 + O_2 + H_2O + N_2O_3 = 2SO_2\begin{matrix}\diagup OH \\ \diagdown NO_2\end{matrix}$$

$$(2)\ 2SO_2\begin{matrix}\diagup OH \\ \diagdown NO_2\end{matrix} + H_2O = 2H_2SO_4 + N_2O_3.$$

The observation that the gases in the first chamber, when the process is working efficiently, are colourless (that is, oxides higher than nitric oxide are absent) led Lunge and Naef to suggest that a considerable part of the action here is the same as that which occurs in the de-nitrating portion of the Glover tower, namely,

$$2SO_2\begin{matrix}\diagup OH \\ \diagdown NO_2\end{matrix} + 2H_2O + SO_2 = 3H_2SO_4 + 2NO.$$

As the latter reaction becomes less intense, practically all the nitric oxide becomes converted into N_2O_3, and thus the colour of the gases in the succeeding chambers is increasingly reddish and completely dark-red in the last chamber.

The temperature of the first chamber is maintained at from 60°–80°, and the gases are allowed to cool until they leave the last chamber at about 40°, the

maximum temperature for efficient working of the Gay-Lussac tower. The most rapid chemical action (probably mainly the de-nitrating action referred to above) takes place in the first half of the first chamber; in the second half, sulphuric acid production is comparatively small, but as the gases become remixed and the nitric oxide becomes more completely oxidised, the action revives in the second chamber and then declines, until at the exit from the last practically no sulphur dioxide remains unoxidised. Correct proportioning of the steam and the amount of oxides of nitrogen present is essential to efficient working of the chamber process; 98 per cent. of the sulphur originally admitted to the system should be converted into sulphuric acid. The process is controlled by frequent analyses of the exit gases from the Gay-Lussac tower, of the inlet gases to the Glover tower and of the chamber acid, nitrous vitriol, and finished Glover acid produced.

The above description of the chambers is intended to indicate the old mode of operation in which the process was supposed to be mainly one of homogeneous gaseous catalysis. Many improvements have been made within the last few decades in order to economise the chamber space; the first of these consisted of the injection of water spray instead of steam into the chambers, when it was found that higher and narrower units could be employed with considerable saving of ground space. Obviously this is equivalent to carrying out more of the reaction in the liquid phase and less in the purely gaseous system.

At about the time that the German sulphuric-acid contact processes were coming into large-scale operation, efforts were made, and have been continued, further to reduce the chamber space. Meyer [16] introduced a system of circular chambers into which the gases were introduced tangentially, in order to induce flow in a spiral direction with consequent intimate mixing. Two very important further modi-

fications out of a number of alternative propositions may also be mentioned :—

The Mills-Packard System.[17]—This consists of circular towers, narrower at the top than at the base, cooled externally by cold water, and fed from the top with a water spray. The towers are usually about 40 ft. high and 15–20 ft. in diameter. This system, in addition to economy in space occupied and in the amount of material (and therefore cost) of the installation, is claimed to tend to more regular and efficient progress of the reactions, and is coming into more and more extended use, both in this country and America.

The Opl Tower.[18]—This system consists of a series of towers, usually six in number, constructed on the lines of a fractionating column, the trays, of course, being made of lead or other acid-resisting material. The hot burner-gases pass into the base of the first tower and from its top to the base of the second, and so on through the whole set of towers in series. The first tower is fed with acid from the second tower, whilst in additon to acid from the succeeding towers water is added to the second, third and fourth, and additional nitric acid is also admitted to the second tower. This procedure again effects great economy in construction and space over the older form of chamber process, and has been increasingly used in the past twenty years on the Continent and also to some extent in England.

In addition to these systems, still more recent devices consist of arrangements by which pools of acid are formed in the chambers or towers through which air is injected (Hurt),[20] or devices for injecting the acid from the later chambers or towers in the form of a mist or spray into the first chamber or tower in order to ensure more efficient contact between the burner gases and the liquid acid spray.[19] Obviously, bearing in mind the corrosive nature and density of the liquids to be handled in the course of the chamber process, the cost of construction and maintenance of

the mechanical devices (acid pumps, elevators, etc.) necessary in these more intensive processes is a factor which has to be placed against the increase in efficiency which is obtained ; for example, the use of an acid-spraying device is probably generally more economical than the practice of injecting air through pools of the liquid acid on account of lower power consumption. It will thus be seen that the engineering and production costs of a modern chamber plant provide many complicated problems, but at the same time there is little doubt that the chamber process would hardly have held its own against the contact process had not the more intensive methods of working been brought into operation.

It will be noticed that the tendency in the latest systems is more and more to carry out the oxidation of sulphur dioxide in the liquid phase, and it is believed that the main reactions which take place under these conditions are represented by the following equations:—

(1) $2SO_2\begin{matrix}OH\\NO_2\end{matrix} + SO_2 + 2H_2O = 3H_2SO_4 + NO$

(2) $2SO_2 + 2NO + 3O + H_2O = 2SO_2\begin{matrix}OH\\NO_2\end{matrix}$

Some idea of the relation between chamber space and the weight of acid produced by the various methods which have been referred to may be gathered from the following table :—

	Cubic Feet Space per lb . Sulphur burnt per Day.	Consumption of Nitrogen Oxides (as lb. nitre per 100 lb. sulphur).
Old . .	16–20	2·5–4
Intensive .	10	1·8–2·7
Mills-Packard	3	1·8–2·0
Opl. . .	2	2·2

Purification and Concentration of Chamber Acid.—The acid coming direct from the chambers is liable to contain various impurities, including traces of lead, iron, arsenic, selenium, and also nitro-sulphonic acid. The Glover acid (commercial or brown oil of vitriol, B.O.V., 78 per cent. H_2SO_4, 140° Tw., 60° Baumé), will contain a still higher percentage of these impurities, including up to 1 per cent. of arsenic, both owing to the fact that concentration has taken place, and also to the removal of impurities from the burner gases with which it is made. Nevertheless this quality of acid is that which is mainly employed for most purposes where special purity is not necessary.

In many other cases, however, it is essential at least to ensure that metals such as arsenic, antimony, lead and selenium are completely absent. This can be effected by passing a current of sulphuretted hydrogen through the chamber acid, when arsenic, antimony and lead are wholly removed as insoluble sulphides, and any selenium present is reduced to the elemental condition; higher oxides of nitrogen are converted at the same time into nitric oxide, which passes away with the excess of hydrogen sulphide. The sulphuretted hydrogen treatment is carried out either in lead-lined scrubbing towers or in mechanical washers; the treated acid is settled and finally filtered through porous earthenware material of the Filtros type.

To convert the Glover acid or brown oil of vitriol into commercial concentrated sulphuric acid (168° Tw. or 66° Baumé), containing 96–98 per cent. H_2SO_4, a further process of concentration is required. This was formerly carried out in fire-heated acid-resisting pans of various types, or by passage of hot gases over the surface of Glover acid contained in shallow troughs, followed by scrubbing the gases through coke towers to remove acid fumes carried forward; this process is still used in some of the smaller works.

The most efficient modern method, however, is that due to Gaillard,[21] who, in 1906, designed what has

come to be known as the Gaillard tower. This consists of a tall tower, about 60 ft. high and 6 ft. in diameter, constructed of masonry, somewhat narrower at the top than at the base, lined with acid-resisting bricks or Volvic lava, and fitted at the top with three atomising jets (Körting jets). The tower is not packed and is fed at the base with flue gases from a coke-producer furnace from which the dust has been settled, and which are at a temperature of about 1,000°. Gases pass up the tower and meet the acid, which descends in a fine spray, after being injected through the Körting nozzles at the top. Concentration of the acid to 96 per cent. H_2SO_4 is readily effected, and the finished acid passes *via* a lead settling tank into a tank supplied with a lead cooling coil. The hot gases from the top of the tower are led to a recuperator consisting of a small lead tower fed with a spray of the original weak acid. This acid, which may form half of the total quantity passing through the main tower, is then admitted to the latter. The gases enter the recuperator at about 200° and leave at 100°–150°, the heat given up being thus utilised to effect some preliminary warming of the acid entering the main tower. A tower of the dimensions given will produce about 40 tons of concentrated acid per day with a consumption of about 3–4 tons of coke. There is a loss of about 3–4 per cent. due mainly to sulphur trioxide carried away by the exit gases after recuperation, but experience in England during the war showed that this could be dealt with effectively by passage of the spent producer gases through a Cottrell electrostatic precipitation plant.

Another modern method which must be mentioned is the cascade process, in which a number of acid-resisting basins are arranged on a series of descending steps constructed in acid-resisting masonry, and heated by means of flues. Hot acid is supplied to the topmost basin and flows in succession down the series, meeting throughout a current of hot air which is passed upwards in the contrary direction. The final concentrated acid

is passed through a lead cooler, settled and stored. Cascade plants are very largely used in the production of the commercial concentrated acid, but the loss as acid fumes is considerably greater than in the Gaillard tower, and may reach 15–20 per cent. Most of this, of course, can be recovered by passage of the exit air from the cascade system through a series of coke scrubbers fed, for example, with chamber acid. The material used for the dishes must be selected with care ; various acid-resisting alloys are available at the present day and, in addition, vessels constructed of fused silica are also largely employed.

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CHAPTER VI

CHLORINE MANUFACTURE BY THE DEACON OR WELDON PROCESSES

THIS chapter is mainly historical, for in it will be described some catalytic processes at one time indispensable for the manufacture of chlorine, but now either fallen into disuse entirely, or definitely on the decline, owing to various factors having combined to make electrolysis the more efficient method. It is true that the processes in question, devised some sixty years ago, were worked out more empirically and, perhaps, by rule-of-thumb methods, than technical catalytic actions of the present day, but they were nevertheless built up by means of sound experimental work, chiefly by chemists associated with one or other of the Lancashire alkali firms which later became the United Alkali Co., who brought them to a high standard of general efficiency.

The factors which have caused the gradual change from catalytic to electrolytic methods are somewhat as follows: At the time that the Deacon-Hurter and Weldon processes were first conceived, the Leblanc salt-cake process was in full operation, and its by-product, hydrochloric acid, was produced in large quantities, for which outlets were sought in various directions. One of these was in the conversion of the acid to bleaching liquor or powder, that is to say, a solution of sodium hypochlorite, or the solid bleaching powder, $CaCl(OCl)$, formed by absorption of chlorine in lime. At that time this was practically the only form in which chlorine was employed on any scale; outside the laboratory there were no uses for chlorine gas, and liquid chlorine was a scientific curiosity. The fact that chlorine produced in the Deacon-Hurter or Weldon-Péchiney processes was a dilute mixture of the gas with

atmospheric nitrogen, etc., was not a serious hindrance to its absorption by lime, but at the present time far more chlorine is employed in the elementary form than as bleaching powder or liquor, and consequently the production of a diluted form of chlorine gas is far less advantageous than the manufacture of practically pure chlorine in bulk.

The recent uses for chlorine, to which reference is made, include its use in the indigo synthesis wherein aniline is condensed with chloracetic acid to produce phenylglycine, and chlorine is required for the chlorination of acetic acid. Still more recent uses which consume very large quantities of liquid chlorine are modern methods of petroleum refining and the chlorination or sterilisation of water supplies (a considerable proportion of the London water supply, for example, is now submitted to this treatment).

The ease with which liquid chlorine or compressed chlorine can now be produced is again connected with general developments in the alkali industry; for, just as the Leblanc process was largely displaced by the Solvay ammonia soda process, so, in turn, this is meeting with increasing competition from electrolytic methods. Even in this country, where electric power is relatively dear, brine solutions can be economically electrolysed in appropriate cells, so as to produce either caustic soda solution or, by the Hargreaves-Bird or similar processes, to give sodium carbonate solution. Chlorine is set free at the anode, in equivalent amount to the alkali obtained from the cathode compartment of the cell, and can be collected in a state of at least 97–98 per cent. purity. The evolved chlorine is carefully dried and compressed into steel cylinders or even into high-pressure tanks mounted on railway waggons. Owing to its relatively high boiling-point and critical temperature liquid chlorine does not present any special difficulty in transport, since its vapour pressure at ordinary temperatures is only of the order of 5–7 atmospheres.

Whereas, for example, the maximum annual world's production of bleaching powder by the Deacon-Hurter process has been estimated at 130,000 tons, equivalent to about 40,000 tons of chlorine, the present annual Continental production of chlorine from one type of cell (the Griesheim Elektron) is approximately 40,000 tons, whilst the annual total chlorine capacity of electrolytic plants in Canada and the United States is at present about 160,000 tons of chlorine, and correspondingly large quantities are produced annually by electrolysis in this country. These figures afford ample evidence of the way in which the older catalytic processes are being supplanted by electrolytic chlorine ; it should also be stated that, although the existing Deacon-Hurter plants are still used for the production of bleaching powder, the latter is also made from electrolytic chlorine, and as the catalytic plants become worn out, they will doubtless in due course be entirely replaced by the electrolytic process.

In consequence of the moribund nature of the catalytic methods, we shall not deal with them in such detail as has been given to sulphuric acid, nitric acid, and ammonia ; we will, however, give in a few words the main points of each of the three catalytic chlorine processes, taking them in decreasing order of efficiency but, as it happens, in the reverse of strict chronological order of their development.

The Deacon-Hurter Chlorine Process.

This method depends on the equilibrium reaction

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

which was first employed on a technical scale by Deacon and Hurter [1] in 1868, and was improved in the succeeding years by these workers in England, and also by Hasenclever [2] in Germany, who introduced the use of purified dry hydrochloric acid in the process about 1883. As already stated, the process, although carefully studied experimentally, was

worked out (so far as modern catalytic theories are concerned) on a purely empirical basis. It was found that several metallic chlorides, notably cuprous chloride, caused the oxidation of hydrochloric acid by oxygen, and that a maximum conversion of the acid to chlorine occurred at about 500°, higher temperatures tending to reduce the yield; the working yield of chlorine obtained in practice, using dry hydrogen chloride, is about 65–70 per cent. Deacon and Hurter took the hydrochloric-acid gas from the salt-cake furnace, mixed it with four times its volume of air and passed it through iron superheaters into iron cylindrical chambers about 12 ft. wide, filled with cuprous chloride impregnated into small pieces of broken brick (the copper content of the catalyst being 0·6–0·7 per cent.); the catalyst vessels were maintained at 450°–500°. The exit gases from the catalyst chambers were passed through earthenware condensers to remove water and unchanged hydrochloric acid, after which the gases were led directly into the bleaching powder chambers. In this simple form of plant the yields varied considerably, and the catalyst rapidly lost its activity. The reason for the latter was found to be partly the volatility of cuprous chloride at the temperature of the reaction and partly the poisoning effect due to oxides of arsenic, sulphur and carbon, and other materials introduced with the gases. Drying the hydrochloric acid gas was found to induce a marked effect on the yield, whilst operation at a somewhat lower temperature (450°) reduced the volatilisation loss of the catalyst.

Thus the later forms of Deacon plant [3] consisted of a system of water scrubbers by which the crude hydrochloric acid was obtained in the form of solution. A current of air was blown through the crude acid and carried the vapour into the base of a tower filled with coke and fed at the top with concentrated sulphuric acid; a pure dry mixture of hydrochloric acid and air was then obtained, which was fed to the

catalyst chamber. The batch of catalyst under these conditions would normally have a life of about three months, at the end of which time volatilisation losses caused the chlorine production to fall below an efficient point; the loss of copper in this way amounted to about 3–4 pounds per ton of bleaching powder made.

At a much later date the equilibria at different temperatures in the action

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$$

were studied by G. N. Lewis,[4] Falckenstein [5] and others, the results obtained confirming the technical practice, in that it was found that the percentage of chlorine at equilibrium diminished with rise of temperature and fell off very seriously above about 600°. At 430°–450°, the lowest temperature at which the cuprous chloride catalyst is reasonably active, the theoretical yield is of the order of 80 per cent. of hydrochloric acid converted to chlorine. Hurter and Deacon concluded from their investigations that the mechanism of the catalytic process depended on the production of an oxychloride as follows :—

(1) $Cu_2Cl_2 + O_2 = CuO.CuCl_2$.
(2) $CuO.CuCl_2 + 2HCl = 2CuCl_2 + H_2O$
(3) $2CuCl_2 = Cu_2Cl_2 + Cl_2$.

Subsequent work has confirmed these views and has also indicated that oxychlorides of other metals frequently give rise to the same series of reactions. Copper chloride, however, is the only one which has been found to give a useful yield of chlorine, that is, to promote the establishment of equilibrium sufficiently rapidly at a temperature low enough to permit of a reasonably high percentage of chlorine at equilibrium.

The Weldon-Péchiney Process.[6]

This process utilises an action somewhat similar to the Deacon-Hurter method :—

$$2MgCl_2 + H_2O + O = 2MgO + 2HCl + Cl_2.$$

It was evolved by Weldon owing to the high losses of chlorine in the original Weldon process, which is described below; although now defunct, it was worked in England, France and Germany to some extent for a considerable period. It was obviously designed to compete against the Deacon-Hurter process and depends, so far as its mechanism is concerned, practically on the alternate production of magnesium oxychloride and magnesium chloride.

The process consisted in evaporating a solution of magnesium chloride with powdered magnesium oxide in proportions to give the oxychloride $MgO.MgCl_2$. The solid oxychloride was powdered, dried at 300° and then passed into brick furnaces maintained at about 1,000°, in which it met a current of hot air. The above reaction then occurred, the mixture of chlorine, hydrogen chloride and residual air being separated as in the Deacon-Hurter process, and the hydrochloric acid employed in the production of fresh magnesium chloride.

The Weldon Process.[7]

This method came into use almost at the same time as the original Deacon-Hurter process and consisted substantially of the following series of reactions :—

(1) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$.
(2) $MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$.
(3) $2Mn(OH)_2 + O_2 + Ca(OH)_2 = CaO.2MnO_2 + 3H_2O$.
(4) $2CaO.MnO_2 + 2Ca(OH)_2 + MnCl_2 + O_2 = 2(CaO.2MnO_2) + 2CaCl_2 + 2H_2O$.
(5) $CaO.2MnO_2 + 2HCl = 2MnO_2 + CaCl_2 + H_2O$.

The " catalyst " in this process may therefore be looked upon as oxides of manganese in varying stages of oxidation. The drawback of the process is that in the course of reconversion of the manganous salt to manganese dioxide, considerable quantities of chlorine are wasted in the production of the by-product calcium chloride, as much as nearly 60 per cent. of the original hydrochloric acid being ultimately

transformed into calcium chloride. Nevertheless, for a certain period, the process was able to compete fairly successfully with the Deacon-Hurter process, because in addition to producing chlorine it served to convert the natural mineral manganese dioxide or pyrolusite into the finely precipitated form known as Weldon mud, which was a much more useful and reactive form of the dioxide for service in the further manufacture of permanganates, manganates and similar oxidised manganese compounds. Commencing with the natural manganese dioxide ore, this was heated in special stoneware stills with concentrated hydrochloric acid, and the chlorine initially evolved led away or finally blown out with air for production of bleaching powder. The acid solution of manganous chloride in the stills was neutralised with natural chalk and settled in tanks, after which the neutral salt solution was pumped into an elevated storage tank from which it was charged into an oxidiser, which consisted of a tall vertical vessel kept at about 55°–60° with a current of live steam. In this vessel sufficient milk of lime was added to precipitate all the manganese as manganous hydroxide and to give, in addition, a 30–40 per cent. excess of lime. The presence of this excess of lime is essential for the ensuing oxidation, since the manganous hydroxide is not quantitively converted to manganese dioxide in presence of air, except under alkaline conditions (that is, so that calcium manganite is formed). The oxidation of the alkaline liquor was effected by blowing a current of air through the tank, when the action (3) took place. A further charge of liquor was then added and the second oxidation (4) carried out, thus producing a combination in which twice as much manganese dioxide was combined with the lime as in the first stage. The finished suspension was then passed to settling tanks and the Weldon mud recovered either for further oxidation to manganates, etc., or for neutralisation and re-use in the chlorine process.

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CHAPTER VII

VARIOUS HYDROGENATION OR DEHYDROGENATION PROCESSES IN PRESENCE OF REDUCED METALS

In addition to the well-defined and important industries already dealt with, such as the manufacture of hydrogen, ammonia, nitric acid or sulphuric acid in presence of a reduced metal, there remain to be considered a number of other instances of technical processes which consist in the interaction of molecules in the gaseous phase at a metallic surface, and which depend essentially on either the addition or withdrawal of hydrogen.

We shall consider in this chapter such processes as the removal of organic sulphur compounds from coal-gas, water-gas or other types of gaseous fuel ; the removal of small quantities of carbon monoxide from similar gas mixtures ; and, finally, certain processes connected with the simpler alcohols, namely, the conversion of the latter into aldehydes or ketones by dehydrogenation, and conversely, their production by hydrogenation of the corresponding aldehydes or ketones.

Removal of Organic Sulphur Compounds from Coal-Gas.

In carbonising coal gaseous sulphur compounds are always produced, principally emanating from pyrites or other inorganic sulphide present in the original coal. The gaseous sulphur compounds are mainly present as sulphuretted hydrogen, whose catalytic removal by oxides receives attention in the next chapter. In addition there are organic sulphur compounds produced, chiefly carbon disulphide, carbon oxysulphide and a certain amount of organic sulphides and mercaptans. The removal of the organic sulphur compounds is much more difficult than that of the free

sulphuretted hydrogen, and it is only within the last twenty years that really satisfactory processes to this end have been devised. The old system of removing hydrogen sulphide by lime also eliminated a certan proportion of combined organic sulphur compounds, but the process was not by any means complete.

The basis of modern procedure for almost complete elimination of combined sulphur from coal-gas rests upon the work of Vernon Harcourt,[1] who many years ago, in the course of his work as gas examiner, devised a laboratory method for the analytical determination of the total combined sulphur in coal-gas. This consisted in passing a defined volume of the gas through a heated tube or other receptacle containing pumice which had been impregnated with a solution of platinum chloride and reduced. By this means all organic sulphur compounds were converted into free hydrogen sulphide, which was then estimated colorimetrically or otherwise. The action in the case of carbon disulphide, for example, may be represented as

$$CS_2 + 2H_2 = 2H_2S + C,$$

whilst a mercaptan of the general formula R.SH would be attacked as follows :—

$$R.SH + H_2 = R.H \text{ (hydrocarbon)} + H_2S.$$

Harcourt, indeed, suggested that the analytical process might be modified for technical purposes by passing the heated gas from the retorts through a mass of heated iron turnings or similar material, but nothing appears to have come of the suggestion. It is obvious, of course, that in dealing with a material such as coal-gas, the cost of treatment must be kept extraordinarily low, and a process which involved, for example, an extra cost of 1*d.* per thousand cubic feet would be regarded with considerable disfavour. The use of costly catalyst or plant, unless either of these are practically imperishable, is therefore out of the question.

There are, however, at least three systems which have been proposed for economic catalytic removal of organic sulphur compounds from coal-gas, and two of these have been in operation on a very large scale.

About twenty years ago the South Metropolitan Gas Co. commenced investigations on the use of nickel for catalytic removal of sulphur, and in 1914 and 1915 Carpenter [2] and Evans [3] gave detailed accounts of the results which had then been obtained. The most suitable catalytic material for this particular purpose was found to be balls of fireclay which were impregnated with nickel chloride, dried and charged into the catalyst retorts. The process is carried out at 450°, and nickel produced at this temperature from the chloride by reduction in coal-gas causes the organic sulphur compounds to be decomposed in exactly the same way as in Harcourt's platinum process. The carbon produced is deposited over the catalyst, and in consequence the amount of action progressively declines ; the plant has therefore to be so arranged that one or more catalyst units are periodically out of action whilst the deposited carbon is burned off by passage of hot air over the spent catalyst. This process effects sufficiently complete removal of the carbon to permit the nickel again to function efficiently in decomposition of the sulphur compounds.

Two very large plants have been erected for the operation of this process, one dealing with 10 million, and the other with 15 million, cubic feet of gas per day. The economics of the process were found to depend not so much on the original capital cost of the plant, or on the cost of the catalyst and its periodical recuperation, as upon the heat consumption necessary to raise the gas to the temperature of 450°, at which the reaction proceeds. This factor, however, was dealt with satisfactorily by means of an elaborate system of heat interchangers whereby the gas. after passage through the catalyst chamber, transfers its heat to untreated gas which is coming

forward towards the catalyst. In the second plant mentioned, which deals with 15 million cubic feet of gas per day, the daily consumption of coke is somewhat over five tons, whilst about 1,300 lb. of metallic nickel is contained in the catalyst chambers. The average reduction of the sulphur content in the coal-gas is about 80 per cent., and the treated gas contains from 6–8 grains of sulphur per 100 cubic feet, whilst its illuminating power is unimpaired; the average cost of the process is estimated at not more than 0·3*d.* per 1,000 cubic feet.

Somewhat prior to the work just recorded, a process [4] had been worked out in the United States on lines more nearly analogous to the original proposals of Vernon Harcourt. The plant proposed consisted of two superheaters filled with chequer work, as in a water-gas plant, with a gas-producer in between. Each superheater is employed alternately in the purification of coal-gas, which takes place at a much higher temperature than in the South Metropolitan process (*e.g.*, from 700°–900°). This temperature is attained by burning producer-gas in that superheater which, at the moment, is not being used for coal-gas purification. Preheated coal-gas is then passed through it until the temperature declines below the lower limit mentioned, when the unit is again subjected to the heating process. In the meantime the second unit has been re-heated by producer-gas and is ready to deal with coal-gas. Carbon deposited on the reduced iron and ironwork of the unit is periodically removed by passage of a current of hot air. This process has been worked on an extensive scale and causes considerable reduction in the content of combined sulphur, the stated average reduction of the latter being about 70 per cent., and the average cost of working being in the neighbourhood of $\frac{1}{2}d.$ per 1,000 cubic feet.

The other process referred to for the removal of organic sulphur compounds from coal-gas was proposed by Guillet [5] in 1912, and consisted in passing

coal-gas over iron oxide instead of a metallic catalyst, at temperatures between 80° and 200°. Since this process is technically a logical development of the ordinary iron-oxide purification of coal-gas, it is discussed in connection with the latter in the next chapter (p. 197).

Removal of Carbon Monoxide from Gases by Hydrogenation or Selective Oxidation.

It has been mentioned in previous chapters that hydrogen originating from water-gas is liable to contain small amounts of carbon monoxide, which is toxic to many of the catalysts used in technical processes. When present in concentrations of the order of 2 or 3 per cent. or more, it is conveniently removed to a large extent by scrubbing under pressure through solutions of ammoniacal copper salts (*cf.* this Section, Chapter II, p. 83); when it is only present in quantities not exceeding, say, 0·5 per cent., this procedure is hardly economical, and removal of these small proportions is better effected either by hydrogenation to methane or by oxidation to carbon dioxide.

The hydrogenation of carbon monoxide [6] can be carried out very simply by passage of the preheated gas over a suitable nickel catalyst at about 300°; methane, which is produced in equal volume to the carbon monoxide originally present, is quite inert to the ordinary catalysts, and merely acts as a diluent of the hydrogen. With repeated use of the hydrogen, however, the concentration of the methane, of course, mounts up, and the hydrogenating action may be retarded simply in consequence of the lowered concentration of the hydrogen in the gas mixture. Removal of small quantities of carbon monoxide from hydrogen by this process is effected by preheating the gas in a nest of cylindrical tubes to about 300°, and then passing it through a catalyst chamber maintained at the same temperature. The latter may consist of one or more tubular retorts into which has been packed a granular

mass such as pumice or small pieces of firebrick impregnated with a solution of nickel nitrate, which has been previously gently calcined to yield the oxide. The latter is rapidly reduced at 300°, and yields a surface of active nickel which completely converts carbon monoxide at the concentrations mentioned into methane. If the hydrogen has been thoroughly purified from sulphur compounds, etc., the nickel will retain its activity for a very long period ; but traces of sulphur compounds in the hydrogen will cause a more or less rapid de-activation of the catalyst, rendering its renewal necessary at more frequent intervals.

An alternative process, which has the relative advantages of demanding a lower temperature, of being somewhat less susceptible to sulphur poisoning, and of furnishing as a product the easily removable carbon dioxide, consists in the selective oxidation of carbon monoxide at the surface of certain mixtures of metallic oxides. This process may be dealt with here, since the catalysts concerned are as much metals as metallic oxides ; that is to say, the process consists in alternate reduction of the metallic oxide by carbon monoxide and its re-oxidation by small amounts of added oxygen present in the gas.

This method was developed more or less independently during the war period by both English and American workers, partly with reference to the technical purification of commercial hydrogen and partly in connection with the manufacture of respirators for dealing with poisonous gases. The work of Harger and Terry,[7] and of Rideal and Taylor,[7] deals more particularly with the former problem, and consists in mixing with commercial hydrogen a small amount of air, sufficient to oxidise from about three to five times the volume of the carbon monoxide present. The mixture is passed over a catalyst which consists of precipitated iron oxide containing about 2·5 per cent. of chromium oxide and about 0·5 per cent. of cerium oxide, at a temperature of 150°–200° ; the carbon

monoxide is much more readily oxidised than the hydrogen under these conditions, and the loss of hydrogen due to simultaneous combustion of the latter is therefore comparatively small. Lamb [8] and his co-workers in America devised a catalyst consisting of 60 per cent. manganese oxide and 40 per cent. copper oxide (termed Hopcalite), and found that this acted as an efficient oxidant for carbon monoxide present in small concentration in air at the ordinary temperature. A gas respirator, for example, charged with Hopcalite, was found to offer useful protection against atmospheric air contaminated with carbon monoxide. They subsequently showed that the same catalyst was effective at temperatures not exceeding 100° for the removal of carbon monoxide from hydrogen, the crude hydrogen being mixed with a small determined percentage of air, as in the Harger process, and passed over the mixed copper-manganese oxide catalyst.

Production of Aldehydes and Ketones by Dehydrogenation of Alcohols.

Certain aldehydes and ketones, particularly the former, are of considerable technical value at the present day, but in a number of cases their production by the ordinary processes of oxidation, etc., is difficult to control, and good yields of the desired products are not always forthcoming. A very useful, if minor, application of catalysis is the passage of the vapour of a suitable alcohol over a metallic catalyst, usually either copper or nickel, when decomposition occurs, a molecule of hydrogen being liberated together with a molecule of an aldehyde (from a primary alcohol) or a ketone (from a secondary alcohol). The utility of this reaction may be gathered from discussion of the technical production of formaldehyde, acetaldehyde, butyric aldehyde and methylethylketone from the corresponding alcohols.

Formaldehyde.—The case of formaldehyde stands a little apart from the others in so far that it has not

yet been found feasible to produce this substance by simple dehydrogenation of methyl alcohol; dehydrogenation of methyl alcohol occurs extremely readily in presence of prepared copper at 250°–300° or of prepared nickel at a somewhat lower temperature, but the formaldehyde which is produced is further attacked and the yields obtained are only of a very small order. In this case, therefore, recourse is had to oxidation rather than simple dehydrogenation, and a mixture of methyl alcohol and air is passed over prepared copper under carefully controlled conditions. Many processes for carrying out this reaction have been patented, but the fullest details of the process in its present form have been given by Orloff.[9] The general operation of the formaldehyde plant on these lines may be described briefly as follows: The catalyst consists of fine metal gauze, either of platinum, silver, silver-copper alloy, or, most usually, of copper alone. Formaldehyde is an intermediate product in the oxidation of methyl alcohol, and it is obvious that, given sufficient oxygen, further transformation of the aldehyde to formic acid, or even to carbon dioxide and water, will take place equally readily, or more readily, than the desired oxidation. Consequently the temperature of the catalyst must be maintained within exceptionally narrow limits, and also the time of contact of the interacting gases with the catalyst must be cut down to the value which is found to lead to the highest yield of formaldehyde. The time of contact depends, of course, upon the rate of flow of the mixed gases and the length of the layer of catalyst to which they are exposed. In practice, the layer of catalyst employed is extremely short; for example, if rolls of 15-mesh copper gauze are used, the layer may be about 120 mm. in length, whereas, with finer gauze of 100 mesh, a length of 70 mm. is found to be better. In Orloff's apparatus the catalyst chamber is built up of a very large number of copper tubes, set concentrically in two copper plates. Each

tube is 80 cm. long and contains a closely-fitting glass tube, 30 cm. long and about 1·5 cm. diameter, in which is placed a 12 cm. length of closely-rolled copper gauze. The catalyst is heated up to the requisite temperature by preliminary ignition of the reacting gases by a sparking device, after which the temperature is maintained by the exothermal nature of the action, and is adjusted to the rate of flow of the mixed gases. A catalyst unit comprising six concentric rings of tubes as described (169 in all) will deal with about 17 kg. of methyl alcohol per hour and produce therefrom about 19 kg. of commercial formalin (40 per cent. formaldehyde).

The proportion of air to methyl alcohol and the rate of flow of the mixture have been studied exhaustively both by Orloff [9] and by Le Blanc and Plaschke,[10] and it appears that, with copper catalyst at 450°, the highest yield of formaldehyde results when one volume of methyl alcohol and 0·315 volumes of oxygen are present, whilst the highest conversion of methyl alcohol to oxidised products requires 0·39 volumes of oxygen for one volume of methyl alcohol. It will be seen, therefore, that either a formalin solution will be obtained containing some unchanged methyl alcohol or the yield of formaldehyde will suffer if complete oxidation of the methyl alcohol is secured. The process is generally carried out so that the highest yield rather than the highest conversion is obtained, and, so far as possible, unchanged methyl alcohol is recovered from the products of oxidation by passage of the latter through a fractionating column.

In operating the formaldehyde plant, methyl alcohol (which should be as free as possible from acetone and water) is fed into a small tank in which it is warmed to about 40° or 50° by means of a closed coil; a current of compressed air is injected into the warmed methyl alcohol at such a rate that the catalyst chamber is maintained steadily at 450° by the heat of oxidation. By adjustment of the temperature of the methyl

alcohol in the tank, the proportions of methyl alcohol and air passing on to the catalyst chamber are maintained so that there is 0·32 volumes of oxygen present for every volume of methyl alcohol vapour. The methyl alcohol-air mixture passes from the mixing tank directly into the catalyst chamber, where the greater part of the methyl alcohol is converted to formaldehyde with a minimum of more intensive oxidation. The exit gases from the catalyst pass into the lower part of a plate fractionating column, when an aqueous solution of formaldehyde separates and is run off from the base of the column (the water having been produced concurrently in the oxidation). Unchanged methyl alcohol vapour, a little formaldehyde, and any carbon dioxide pass through the column, and the methyl alcohol is subsequently condensed and returned to the process. The aqueous formaldehyde solution separated at the base of the main fractionating column constitutes commercial " formalin," and should contain 38–40 per cent. of formaldehyde with not more than 10–12 per cent. of methyl alcohol.

A recent patent of the I.G. Farbenindustrie [11] A.–G. claims the production of 60 per cent. formalin solution by a similar process of oxidation in which completely anhydrous methyl alcohol is employed.

Ordinary 40 per cent. formalin is manufactured on a fairly considerable scale, and is used on the one hand as an important antiseptic and disinfectant and on the other in commercial synthetic organic chemistry, especially in the production of certain dyestuffs (for example, of the acridine series) and also of a number of fine chemicals, the most familiar of which is probably hexamethylenetetramine or " hexamine," a condensation product of six molecules of formaldehyde with four molecules of ammonia. It is also required in quantity for the manufacture of synthetic resins by its condensation with phenols (Bakelite, p. 337) or urea.

Dehydrogenation of Ethyl Alcohol and Higher Alcohols

in presence of Metallic Copper.—The remaining lower alcohols of the ordinary aliphatic series are readily converted into corresponding aldehydes or ketones by passage over reduced copper [12] at about 300°, a process which has been employed technically for the preparation of several aldehydes and ketones of commercial interest. Nickel is more active than copper as a dehydrogenating catalyst, but it has the disadvantage that it exercises further action on the carbonylic derivatives formed and tends to produce carbon monoxide and saturated hydrocarbons; for example,

$$CH_3CHO \longrightarrow CH_4 + CO.$$

Copper, at the temperature indicated, does not give rise to this complication, and moreover it can be prepared conveniently in a form which permits of periodical recuperation by simple oxidation in a current of hot air. The production of copper in this form has been described by Legg and Adam [13] and consists in the manufacture of fused cuprous oxide, either by melting down ordinary black copper oxide or by burning copper turnings in a current of air heated to about 1,200°. The solidified cuprous oxide forms a hard brittle crystalline mass of a bluish-black colour, which can easily be broken down into granules of any desired size, for example $\frac{1}{4}$–$\frac{3}{8}$ in. mesh. This oxide has the great advantage of being reducible at a low temperature (220°–300°), and of retaining its external size after reduction, although the density of the metallic copper produced is considerably higher than that of the oxide. In other words, a very porous mass of spongy copper is obtained which is of considerable catalytic activity; the combination of porosity and hard granular structure renders it particularly suitable for use as a vapour catalyst.

In producing an aldehyde or ketone by means of this catalyst, the appropriate alcohol is first of all volatilised from a still and the vapour passed through a series of heated copper tubes in order to bring it

to a temperature of 300°, or somewhat higher, the conversion of an alcohol to an aldehyde or ketone being an endothermic action. The pre-heated vapours then pass into a tubular retort (or retorts) packed with the cuprous oxide prepared as described. If the alcohol employed is of low molecular weight, for example, ethyl alcohol or isopropyl alcohol, the cuprous oxide is reducible by the alcohol at 280°–300°, and it is unnecessary to carry out a preliminary reduction in hydrogen (a procedure which may be necessary in the case of certain of the higher alcohols); with ethyl alcohol, the cuprous oxide is reduced almost quantitatively according to the equation.

$$Cu_2O + CH_3CH_2OH = 2Cu + H_2O + CH_3CHO.$$

The dehydrogenation process is usually incomplete at 300°, but if higher temperatures are employed side reactions complicate matters to a considerable extent; for example, at 350° or higher, ethyl alcohol yields not only acetaldehyde, but increasing amounts of carbon dioxide, carbon monoxide and saturated and olefinic gaseous hydrocarbons, in addition to products of polymerisation of the aldehyde, which are deposited on the catalyst and hinder the process. It is therefore desirable to conduct the operation at the lower temperature and obtain a maximum yield of aldehyde or ketone rather than the maximum decomposition of the alcohol present. The vapours emerging from the catalyst chamber thus consist of a mixture of aldehyde (or ketone) with unchanged alcohol, hydrogen in equimolecular proportion to the aldehyde (or ketone) produced, and 1 or 2 per cent. of oxides of carbon and gaseous hydrocarbons. The whole mixture is conveniently passed into a fractionating column heated by live steam and constructed in two sections, in the first of which the unchanged alcohol is separated from aldehyde (or ketone) and hydrogen, condensed and returned to the process. The lighter constituents of the mixture pass through to the second column,

where the last traces of alcohol are eliminated and returned to the first column, whilst the aldehyde or ketone is condensed continuously at the top of the second column ; hydrogen and permanent gases pass on through a water scrubber in which the last traces of aldehyde or ketone are separated. The operation of such a column is similar in general principle to that of the ether-alcohol column, which is described in some detail in Section IV., Chapter III, p. 330.

This process has been employed technically in the following cases :—

Acetaldehyde has been produced from ethyl alcohol on a large scale, although as a general rule economic considerations render acetylene a more suitable raw material than alcohol for the production of this aldehyde (*cf.* Section IV., Chapter I, p. 288). The optimum yield of acetaldehyde is obtained at temperatures not exceeding 300°, when about 20–25 per cent. of the alcohol present is converted into acetaldehyde at each passage over the catalyst ; the remainder is recovered by fractionation, as described, and at the same time acetaldehyde of a high degree of purity is withdrawn from the top of the column. The overall yield of acetaldehyde from ethyl alcohol by this process is about 90–92 per cent. Minor amounts of ethyl acetate and other condensation products of acetaldehyde are produced in addition to a small percentage of permanent gases, and the catalyst slowly declines in activity owing to deposition of a layer of complex condensation products. After twenty-four to forty-eight hours' use it is expedient to interrupt the process and reoxidise the copper superficially in a current of hot air when, on subsequent reduction at or below 300°, its activity is fully restored.

Propyl alcohol and isopropyl alcohol are equally readily dehydrogenated respectively to propionic aldehyde and acetone, but this is of theoretical rather than of technical interest. On the other hand, *normal butyl aldehyde* has been produced from normal butyl

alcohol [14] by the copper process, the conversion to aldehyde at 300°–320° being in this case of the order of 80–90 per cent.

It has also been suggested [15] to manufacture *methylethylketone* by similar dehydrogenation of methylethylcarbinol (isobutyl alcohol), the conversion again being relatively large in presence of copper at 300°. It should be pointed out that by a sequence of catalytic processes it is possible to pass from normal butyl alcohol to methylethylketone in the following three stages :—

$$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH{:}CH_2 \longrightarrow$$
$$CH_3CH_2CH(OH).CH_3 \longrightarrow CH_3CH_2COCH_3.$$

Certain hydro-aromatic alcohols also lend themselves to this reaction ; for example, cyclo-hexanol [16] and the methyl cyclo-hexanols (produced from phenol or the cresols by hydrogenation, *cf.* p. 229) are rapidly converted into the corresponding cyclo-hexanone or methyl cyclo-hexanones in presence of copper at 300°. The same process can also be applied to borneol,[17] from which camphor is obtained in good yield on dehydrogenation.

Production of Alcohols by Hydrogenation of Aldehydes or Ketones.

This action is the reverse of that with which we have just dealt, and may prove to be of technical utility in a number of cases. The same metals as those employed in dehydrogenation are effective for reduction of aldehydes or ketones,[18] but the change takes place at a lower temperature and, in general, it is found that nickel is a more efficient catalyst in this case than copper. The nickel catalyst may be employed on a porous support (for example, pumice impregnated with the nickel salt and reduced), or better, in the form of activated nickel turnings of the type devised by Bolton and Lush [21] (*cf.* p. 221). Certain high-boiling ketones or aldehydes are hydrogenated to the corresponding alcohols in the liquid

state (a subject which is dealt with in Chapter IX of this section, p. 234), and the only cases of production of alcohols by hydrogenation in the vapour phase which we need mention specifically are those of ethyl alcohol and isopropyl alcohol.

Ethyl Alcohol.—The production of ethyl alcohol from acetaldehyde has been shown to be technically practicable on a large scale in Switzerland,[19] but at present the cost of alcohol derived in this way from acetylene does not compete under the most favourable conditions with that of fermentation alcohol. In view of the wide number of other technically valuable products which can be obtained from acetaldehyde it is doubtful whether, even if supplies of fermentation alcohol failed, this method of preparation would compete with, for example, the recovery of alcohol from waste gases containing ethylene (*cf.* Section IV., Chapter I, p. 303).

The hydrogenation of acetaldehyde has been carried out in Switzerland in presence of nickel deposited on pumice as employed by Sabatier,[18] and undoubtedly the above-mentioned Bolton and Lush [21] catalyst would serve the purpose even better. The layout of an aldehyde reduction plant is similar to that employed in other vapour catalyses with the exception that, in this instance, it is more necessary to secure rapid and adequate removal of the heat of reaction than to preheat the interacting gases to the required temperature. Any increase of temperature beyond about 150° causes considerable destruction of acetaldehyde in presence of nickel, and therefore the temperature of the system must be kept definitely below this point, whilst it is also found best to conduct the process in presence of a very large excess of hydrogen.[20] The Elektrizitätswerk Lonza[19] also recommends that the hydrogen should contain 0·3 per cent. of oxygen, as this tends to restrain the production of ethyl ether as a by-product. On a large scale overall yields of 90 per cent. of ethyl alcohol from acetaldehyde have been consistently obtained by this process.

Isopropyl Alcohol has come into favour of late years as a substitute for ethyl alcohol in the production of perfumes; it can be made from acetone at a price which compares more or less favourably with that of ethyl alcohol, especially in view of the fact that the question of excise duty is avoided to a considerable extent. Acetone, produced either by fermentation from starch or chemically from acetic acid, is mixed with excess of hydrogen and passed over nickel, as in the preceding case, but at a temperature of from 150°–180°. The process is conveniently carried out under pressure, when the rate of reaction and the ease of condensation of the isopropyl alcohol produced are both increased By employing high pressures it should be readily possible to effect hydrogenation of acetone in the liquid condition at, say, 120°–140°, but so far as the writer is aware, isopropyl alcohol at present manufactured by this method is produced by catalysis in the vapour phase. Although the demand for isopropyl alcohol is still small compared with that for either acetic acid or acetone, it is increasing steadily and the compound is being produced by several manufacturers of fine chemicals in America, on the Continent, and to some extent in this country

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CHAPTER VIII

INTERACTION OF GASES OR VAPOURS CONDITIONED BY METALLIC OXIDES

In most of the processes discussed in the preceding chapters the catalytic agent was a metal prepared in suitable form. In a number of cases, however, oxides of the metals exert specific influence on the course of chemical change, and a few of these are used, although not so widely as metal catalysts, on a manufacturing scale.

Often the action of a metallic catalyst is connected to some extent, although not exclusively, with its capacity for adsorbing hydrogen, so that catalyses by metals can usually be placed in the categories of hydrogenation or dehydrogenation. The metallic oxides display little tendency to act simply as hydrogenating or dehydrogenating catalysts; they are more usually concerned either in the removal of the elements of water from organic compounds or in processes of more or less simple oxidation (as distinct from dehydrogenation)—processes, for example, such as the oxidation of sulphuretted hydrogen to sulphur or sulphur dioxide and of aromatic hydrocarbons to oxygenated derivatives.

The extent to which such processes are used at the present time varies very considerably. One example of this type of action is used on an enormous scale in most coal-gas installations, where sulphuretted hydrogen is removed from the crude gases by passage through iron-oxide purifiers. Another instance which is becoming increasingly important is the oxidation of naphthalene to phthalic anhydride, or of anthracene to anthraquinone, by passage of a mixture of the respective hydrocarbon vapours with air over a heated oxide or

mixture of oxides such as those of vanadium or molybdenum. Some indication of the possibilities of this type of contact action will be gathered from the typical cases which will be discussed briefly in the present chapter.

Dehydration of Alcohols to Olefines or Ethers.

In the later stages of Sabatier's investigations on the catalysis of organic compounds at solid surfaces, attention was paid to the dehydrating and dehydrogenating activity of a large number of metallic oxides. This aspect of the subject was especially studied by Sabatier and Mailhe,[1] who found that, for example, ethyl alcohol was converted into ethylene and water or, alternatively, into hydrogen and acetaldehyde, by the oxides quoted in the following table. The third column shows the percentage of ethylene in the mixture of gases produced when ethyl alcohol vapour was passed over the respective oxides at 340°–350° :—

		Per cent. C_2H_4.	c.c. per min.
Thoria	ThO_2	100	31
Alumina	Al_2O_3	98·5	21
Oxide of Tungsten (blue) .	W_2O_5	98·5	57
Chromium oxide . . .	Cr_2O_3	91	4·2
Silica	SiO_2	84	0·9
Titania	TiO_2	63	7·0
Zirconia	ZrO_2	45	1·0
Uranium oxide . . .	UO_2	24	14
Ferric oxide (initial) . .	Fe_2O_3	14	32
Vanadium oxide . . .	V_2O_3	9	14
Zinc oxide	ZnO	5	6
Tin oxide (initial) . .	SnO	0	45
Manganese oxide (initial) .	Mn_3O_4	0	12
Cadmium oxide (initial) .	CdO	0	11·2
Magnesium oxide . .	MgO	0	Traces.

From this table it is clear that thoria, alumina, and the oxides of tungsten and chromium are pre-eminently

dehydrating catalysts, whilst a large number of others promote both types of decomposition; finally a few oxides, notably those of zinc, tin, cadmium and manganese, are almost exclusively catalysts of dehydrogenation. From a technical standpoint it is necessary, of course, not only to consider the relative proportions of the two types of reaction, but also to bear in mind the intensity of the change set up by any given oxide. As a matter of fact, the dehydrogenating oxides are almost wholly of feeble or evanescent activity, and no serious suggestion has yet been made to utilise them in technical practice, for example, in the production of an aldehyde or ketone from an alcohol. Again, those oxides which give rise to a mixed effect are obviously not likely to be suited to the production of a definite technical product, although it may be observed that so far as relative activity is concerned, some at any rate of this class are considerably more active than the hydrogenating oxides just mentioned. There remains the more or less exclusively dehydrating type of metallic oxide catalyst, and here certain of these, especially silica, alumina and thoria are, when prepared with due regard to the condition of the exposed surface, of very high activity.

It should be made clear, however, that, so far as the writer is aware, none of these dehydrating oxides has been used hitherto in the manufacture of olefine hydrocarbons or ethers. When, for example, ethylene is required to be produced from alcohol in quantity, it is probably nearly always made by the catalytic action of sulphuric or phosphoric acids as described in Section IV., Chapter III, p. 332. The methods which are indicated below, therefore, are to be regarded rather as indications of procedure potentially available than of processes actually in being; consequently it is not necessary to discuss them at any length. The oxides employed by Sabatier and Mailhe were prepared as a rule by precipitation from the nitrate followed by washing and gentle heating, or by gentle calcination of the

nitrate of the metals. The work of Adkins [2] and his colleagues in America on the oxides of aluminium and titanium prepared by different methods, for example from inorganic salts, from the acetates or from ethylates (or other alkyl oxides) of these metallic oxides, shows clearly that considerable differences, not only in the activity but also in the type of action induced, are to be observed according to the method of preparation of the oxide which has been followed. The exact implication of these variations is not fully understood, and reference may be made to the original communications of this author and to further discussion by H. S. Taylor [3] and others on the theoretical aspects of these observations.

Coming to practical details, it may be stated that at temperatures varying between 330° and 450°, ethyl alcohol is transformed more or less quantitatively into ethylene and water in presence of suitably prepared thoria, alumina or silica. Sabatier states that thoria is the most active oxide and also the most suitable under working conditions. Alumina comes next in the series, and it is probable that, if this process were required to be worked technically, economic considerations would decide the case in favour of the latter oxide. The working conditions, which may be foreseen as necessary for carrying out such a reaction, would include the preparation of the oxide catalyst in a form which, whether supported or non-supported, would be sufficiently granular to offer suitably low resistance to the passage of the vapours, and at the same time would possess surface conditions conducive to the exhibition of maximum activity. Furthermore, as in all similar cases, it would be necessary also to pre-heat the alcohol vapour to such a temperature that the temperature in the catalyst chamber itself would be maintained suitably constant and probably not below 350°. According to Sprent,[4] the net yield of ethylene from alcohol by the alumina process is greatest at 360°; above this temperature the

ethylene tends to be decomposed and also the alumina catalyst slowly undergoes change of physical state, thus rendering the surface progressively less active.

It seems reasonable to suppose, in the case of ethylene, that the heat consumption involved in this process must always be considerably greater than that in the alternative sulphuric or phosphoric acid process, which proceeds at about 170° or 180°, and for this reason one cannot foresee any extensive application of the metallic oxide process in this case. In special cases, however, the process might be technically feasible. Thus, in order to convert normal butyl alcohol into iso-butyl alcohol, it has been proposed [5] to pass the vapours of normal butyl alcohol over alumina at about 400°, when the hydrocarbon butylene is produced, and this by treatment with sulphuric acid and subsequent saponification furnishes the corresponding secondary or iso-butyl alcohol.

$$CH_3.CH_2.CH_2.CH_2.OH \longrightarrow CH_3.CH_2.CH:CH_2 + H_2O$$
$$CH_3.CH_2.CH:CH_2 + H_2O \longrightarrow CH_3.CH_2.CH(OH).CH_3.$$

It is, of course, obvious that dehydration of alcohol can take place in two ways, giving either ethylene and water or ether and water. So far as the aliphatic alcohols are concerned, the production of ethers is decidedly the exception rather than the rule, although both Sabatier [1] and Ipatiew [6] state that in presence of alumina at low temperatures (*i.e.* below about 250°) some ether is produced in addition to ethylene. The case is somewhat different, however, with aromatic alcohols and especially with phenols, and it was shown by Sabatier that passage of phenol vapour over thoria or alumina at 400°–450° resulted in the production of considerable amounts of diphenyl oxide (or diphenyl ether). This compound, especially when diluted, has a strong odour reminiscent of geranium leaves, and it is manufactured as a synthetic perfume in some quantity by this process. The conversion of phenol to diphenyl ether is not quantitative, but

this is of little practical detriment since the unchanged phenol can be removed very readily from the neutral ethereal product.

Sabatier and Mailhe also observed that under laboratory conditions mixtures of a phenol with a lower aliphatic alcohol, passed over thoria or alumina under similar conditions to the above, produced a certain amount of mixed ethers, for example anisole, $C_6H_5O.CH_3$, or phenetole, $C_6H_5O.C_2H_5$, from mixtures of phenol with respectively methyl or ethyl alcohols. So far as can be ascertained, however, this process has not been worked on a manufacturing scale.

Production of Ketones from Organic Acids.

Metallic oxides have been used industrially from time to time in the catalytic manufacture of ketones from the simpler organic acids, especially of acetone from acetic acid. The general course of this change, which is a somewhat complicated case of dehydration, is summed up in the equation

$$2R.COOH = R_2.CO + CO_2 + H_2O.$$

The first member of the series of aliphatic acids, formic acid, does not behave strictly in accordance with this equation, and although the process is not utilised technically, it is desirable from a theoretical point of view to consider for a moment the behaviour of formic acid vapour at the surface of typical heated metallic oxides. With metals, as distinct from metallic oxides, it has been noted earlier that two types of decomposition are encountered, namely

$$H.COOH \longrightarrow CO + H_2O$$
$$H.COOH \longrightarrow CO_2 + H_2.$$

The first decomposition is essentially one of dehydration, whilst the second is more comparable with dehydrogenation.

When metallic oxides are employed, the dehydro-

genating action is, as a rule, negligible or completely absent and the main change is primarily in the direction of formation of water and carbon monoxide; in certain cases, however, further interactions occur, in which more than one molecule of formic acid is concerned, with the result that either formaldehyde or methyl alcohol may be produced, whilst instead of carbon monoxide, carbon dioxide appears as a gaseous decomposition product. The course of the action may be understood to a certain extent if we consider that "nascent" carbon monoxide and a second molecule of formic acid interact as follows (although it is most unlikely that carbon monoxide is actually liberated in such cases):—

$$H.COOH + CO = CH_2O + CO_2$$

and in this way the following three alternatives may be formulated:—

$$H.COOH \longrightarrow H_2O + CO.$$
$$2H.COOH \longrightarrow CH_2O + CO_2 + H_2O.$$
$$3H.COOH \longrightarrow CH_3OH + CO_2 + H_2O.$$

Referring to the table on p. 186, the oxides which are most active dehydrating agents for alcohols (*i.e.* alumina, titania, etc.) generally resolve formic acid completely into carbon monoxide and water; oxides lower in the table, especially those of uranium, zinc, and tin,[8] are found to give definite quantities of formaldehyde with, in some cases, a certain amount of methyl alcohol in addition.[7] The temperature of decomposition naturally influences the relative proportions of these products to a marked degree; as a general rule, a temperature of about 300° gives the greatest yield of formaldehyde.

Conditions have not yet been suggested for the production of formaldehyde by this means in yields of commercial interest, but the process is of theoretical significance in that it indicates an alternative synthesis of formaldehyde from coal (water-gas) through formic

acid instead of through methyl alcohol, which holds the field at present :—

$$(CO + H_2) + H_2 \longrightarrow CH_3OH \xrightarrow{O_2} CH_2O + H_2O$$

$$(CO + H_2) \xrightarrow{NaOH} H.COOH \longrightarrow CH_2O + CO_2 + H_2O.$$

It will be observed that the decomposition just referred to is typical of that for the production of ketones from the remainder of the ordinary aliphatic acids. The latter change, of course, is familiar in the dry distillation of, for example, calcium acetate, when acetone, water and calcium carbonate are produced. As early as 1895, Squibb [9] suggested that this process could be made catalytic by passing a current of acetic acid vapour over barium carbonate at a temperature of about 500°. It was found that at least 90 per cent of the theoretical yield of acetone could be obtained in this way, and the method found some technical application in the United States. Later, Ipatiew [10] and Sabatier, Mailhe and Senderens [11] showed that at a somewhat lower temperature (400° or lower) metallic oxides such as those of aluminium, thorium, chromium or zinc, were effective and indicated that equally high yields could be produced. The French scientists also found that passage of a mixture of the vapours of formic and a higher aliphatic acid over alumina led to the production of the corresponding aldehyde ; for example, a mixture of formic and acetic acids yielded a certain amount of acetaldehyde, an action which is again analogous to the preparation of acetaldehyde by distillation of a mixture of calcium formate and acetate.

The function of metallic oxide or carbonate catalysts in this action is thus strictly parallel with the corresponding decomposition of calcium salts of the same acids, and it may be taken for granted that transitory formation of the salt concerned takes place at the catalyst surface or, at least, that selective adsorption (in the chemical sense) of the aliphatic acids takes place at the metallic oxide surface.

Technical Production of Acetone over Metallic Oxide Catalysts.—As already stated, Squibb's process has been used on a technical scale, employing barium carbonate at 500°. The plant used in one form of this process consisted of a rotary kiln 2 ft. in diameter and 12 ft. in length, containing a layer of precipitated barium carbonate and maintained at 450°–500°; this plant was capable of converting 1,700 lb. of glacial acetic acid into acetone in 126 hours with a yield of about 90 per cent. In a later form of catalytic process, the catalyst consisted of alumina precipitated or impregnated on a porous granular support, and somewhat similar results to the Squibb process were obtained at about 480°–500°; a plant of this type, producing two to three tons of acetone per day, was operated for a time during the late war.

The Canadian Electrochemical Products Company at Shawinigan has used a somewhat similar process (referred to again in Section IV., Chapter I, p. 303) with synthetic acetic acid produced from acetylene; the vapour of the acid was led over a catalyst, which consisted of calcium hydroxide with a small quantity of magnesium hydroxide coated on rough cast iron balls and contained in steel tubes 13 ft. long and 1 ft. in diameter. By careful control of the temperature, both in pre-heating the acetic acid vapour and in the catalyst chamber itself, it was found possible to obtain 95 per cent. conversion to acetone at 483°.

At the present time, as a matter of fact, little if any acetone is manufactured by these processes; but this is due solely to the circumstance that sufficient acetone to meet the present demand is available from the fermentation of carbohydrates by means of specific bacteria (*cf.* Section III., p. 270). The fermentation process produces for every part of acetone two parts of *n*-butyl alcohol, a material which is at present in very considerable demand, so that at the moment acetone may be looked upon as a by-product resulting from the manufacture of butyl alcohol.

The investigations of Sabatier and Ipatiew show that other higher ketones may be produced in the same way, but there is little or no technical demand for most of these. It may, however, be mentioned that, as Easterfield and Taylor have shown,[12] the higher fatty acids (for example, palmitic or stearic acid) can be converted in high yield into the corresponding ketones by agitating them in the liquid state at about 300° with siliceous materials, alumina or, preferably, ferrous oxide, whilst Grün[13] states that the action proceeds readily enough in presence simply of massive iron. The ketones thus produced are solids of fairly high melting-point (*e.g.*, from 60°–85°), and may well find application as waxes for various purposes, for which their texture, relative high melting-point, and completely neutral nature would seem to render them suitable; catalytic reduction of the liquid ketones converts them into the corresponding secondary alcohols, which are also wax-like bodies.

Sabatier and his co-workers, again, indicate that aromatic acids can be converted in the vapour phase to the corresponding ketones, but the action apparently proceeds with considerably less ease in the case of these compounds.

Oxidation Processes—Purification of Coal-gas from Sulphur Compounds.

The removal of combined organic sulphur from coal-gas, or rather its conversion into methane (or carbon) and sulphuretted hydrogen, has been discussed mainly in the preceding chapter (p. 168), since it is most usually effected by the hydrogenating action of metals. We have now to consider, however, the removal of sulphuretted hydrogen from illuminating gas, a process which it has been necessary to practise much more rigorously than the former and, indeed, ever since coal-gas was used as a general source of illumination or of heating. Crude coal-gas, after removal of tar, ammonia, etc., in the scrubbing

plant, will contain relatively large amounts (*e.g.*, 0·5–1·5 per cent.) of free sulphuretted hydrogen, whereas the permissible amount of this material in the gas supplied to consumers is strictly limited by law. Originally it was the usual custom to pass the gas over lime purifiers, when calcium sulphide and carbonate were formed and sulphuretted hydrogen and carbon dioxide were removed. Compared with the modern process about to be described, the use of lime is costly, and the disposal of the residual spent lime sludge is difficult and somewhat of a nuisance. More modern practice consists in passing the gas over and through masses of porous iron-oxide ore when, in presence of moisture, actions similar to the following take place :—

$$Fe_2O_3 + 3H_2S = 2FeS + 3H_2O + S.$$

The gas is led through a series of very large cubical or rectangular steel " boxes," which contain a fairly porous form of natural ferric oxide, such as spathic iron ore or bog iron ore, or possibly masses of precipitated ferric hydroxide mixed with sawdust or other light solid in order to render the mass sufficiently permeable to comparatively free passage of the gas. The purification is conducted on the counter-current system, *i.e.*, the crude coal-gas passes first through a box containing nearly exhausted iron oxide and then progressively through the series until, in the final box, it meets with a comparatively fresh charge of the iron oxide. When the charge of ore in a box becomes so far spent that it ceases to absorb sulphuretted hydrogen efficiently, the iron sulphide is re-transformed to ferric oxide with simultaneous production of free sulphur :—

$$4FeS + 3O_2 = 2Fe_2O_3 + 4S.$$

The re-oxidised ore, still containing liberated sulphur, can then be used again quite efficiently in the removal of sulphuretted hydrogen ; and this cycle of operations can be carried on until the ore contains

about 50 per cent. of free sulphur. The fully-spent ore then becomes a quite useful source of sulphur for the manufacture of sulphuric acid, and is by no means a useless waste product. Indeed a considerable amount of the material is, so to speak, hired out to gas undertakings by chemical manufacturers, who eventually burn the deposited sulphur from the fully spent ore, thus using it as raw material in the manufacture of sulphuric acid.

Spent iron oxide has also sometimes been used as a fertiliser, particularly in France, but owing to the presence in it of toxic compounds, it must be applied to the soil well in advance of sowing-time.

It will be seen that this process is semi-catalytic in nature in so far that the iron oxide is used over and over again to carry out the same sequence of chemical changes. In recent gasworks practice it has been made more completely catalytic by carrying out the purification in presence of a small amount of added air. This came about first of all because it was observed that the working life of a given batch of iron oxide ore on the old system varied very considerably, and this was traced to differences in the crude gas (which always contains small but variable amounts of free oxygen). The greater the amount of oxygen in the crude gas, the longer was the efficiency of a purifier box maintained—due, of course, to the fact that both actions expressed in the above equations were proceeding concurrently, so that essentially the chemical action concerned became

$$2H_2S + O_2 = 2S + 2H_2O.$$

It has, therefore, become the practice to mix very small proportions of air with the crude gas and to pass the mixture through the iron-oxide purifiers, thus increasing the working period of a given batch of ore from a few days to many months; in fact, until the free sulphur content of the treated ore becomes sufficiently high to make it of economic value to the sulphuric

acid manufacturer. The operation of this process demands careful chemical control, however, because the sequence of actions culminating in oxidation of sulphuretted hydrogen to free sulphur and water is accompanied by development of considerable heat, and it is necessary so to arrange the proportion of oxygen present, and the velocity of passage of the gas through the purifiers, that no undue increase of temperature takes place.

It has also been found that the use of crude ore is not the most efficient means of carrying out the catalytic action, and it is becoming more and more the custom to employ precipitated iron oxide as described above, or quite frequently, in modern practice, to supplement the use of iron oxide with that of precipitated manganese oxides; that is to say, Weldon mud derived from the catalytic production of chlorine by the Weldon process (*cf.* this Section, Chapter VI, p. 166).

In connection with the above methods (which only affect the amount of free sulphuretted hydrogen present in the gas) one of the proposals for partial elimination of combined organic sulphur (*cf.* preceding Chapter, p. 172) also makes use of something akin to the ordinary iron-oxide purifier. For this purpose, however, the iron oxide must be heated at from 130°–300° when, according to Guillet,[14] carbon disulphide is decomposed in presence of moisture with formation of free sulphuretted hydrogen :—

$$CS_2 + 2H_2O = CO_2 + 2H_2S.$$

The sulphuretted hydrogen formed is, of course, removed by the iron oxide and converted into ferrous sulphide as before, so that intermittent re-conversion of the solid material back to the fully-oxidised form is necessary. It seems possible, however, that the process might be so modified that continuous conversion of the hydrogen sulphide to free sulphur might be arrived at as in the process which has just been described; or, as Rideal and Taylor have suggested,

since it is found that at 500° in the catalytic process for the manufacture of hydrogen from water-gas (*cf.* this Section, Chapter II, p. 83), all sulphur compounds are converted into sulphuretted hydrogen, these conditions may possibly be found practicable in a modified form of the Guillet process. Of course, other things being equal, purification at the lower temperatures suggested by Guillet would be less costly than a process operating at 500°.

The Chance Sulphur-recovery Process.

In the well-known Chance process for recovering sulphur from the alkali waste (calcium sulphides) of the Leblanc soda-ash process, a current of carbon dioxide is passed through a series of scrubbing towers counter-current to a suspension of the alkali waste, whereby all the combined sulphur is removed as hydrogen sulphide :—

$$\begin{cases} CaS + H_2O + CO_2 = CaCO_3 + H_2S. \\ CaS + H_2S = Ca(SH)_2. \\ Ca(SH)_2 + H_2O + CO_2 = CaCO_3 + 2H_2S. \end{cases}$$

The effluent gas is collected, mixed with just sufficient air to provide a ratio of two volumes of hydrogen sulphide to one of oxygen and passed up into a converter known as a Claus kiln, which consists of a producer with a grating on which rests a mass of bog iron ore or similar material. Once combustion has been started locally oxidation proceeds exothermally at the surface of the iron oxide :—

$$2H_2S + O_2 = 2S + 2H_2O.$$

The temperature requires careful regulation, otherwise undesired side reactions set in ; the temperature of the exit gases should not greatly exceed 300° in order to obtain the maximum yield of sulphur.

According to Rideal and Taylor the mechanism of the oxidation in the Claus kiln is the same as that in an ordinary iron-oxide gas purifier in presence of small quantities of oxygen.

Oxidation Processes—Oxidation of Hydrocarbons in Presence of Metallic Oxides.

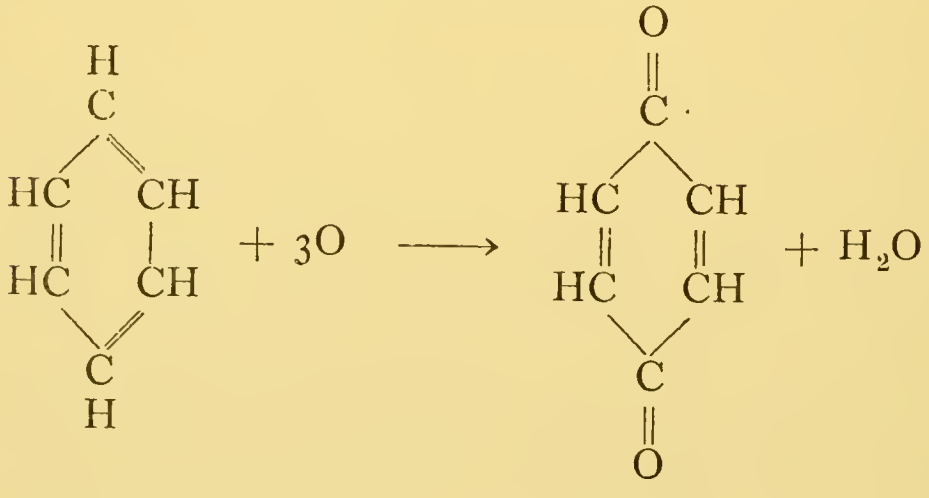
The group of processes about to be described has only been investigated systematically since about 1916, but it would appear that many important reactions may well be developed in the future on the basis of the work which has been carried out during that period, notably by the Barrett Co. of New York, Weiss and Downs, the British Government Fuel Research Board, and other groups of workers.

The work of the Fuel Research Board has dealt largely with the possibilities of oxidising simple aliphatic hydrocarbons, such as those present in fuel gases, in order, for example, to produce formaldehyde. A report on the general results obtained has been published by Ledbury and Blair,[16] who show that, so far as this particular proposition is concerned, it does not appear that there is any immediate likelihood of the formaldehyde produced in this way competing with that produced from coal through the intermediate agency of water-gas and methyl alcohol.

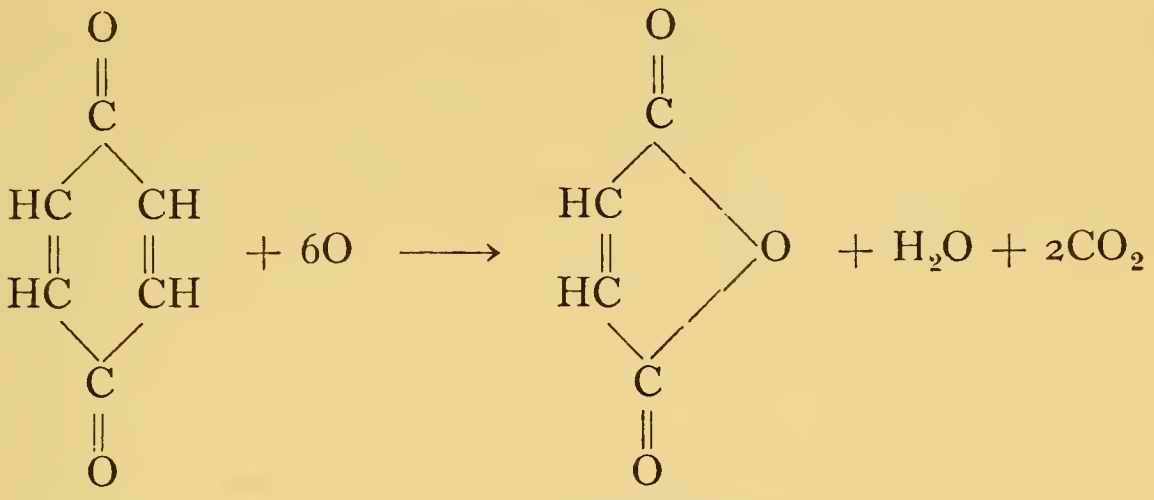
The phase of these processes which is at present most interesting is that of the controlled oxidation of aromatic hydrocarbons into products of technical value, by passage of a mixture of the hydrocarbon vapour with air over certain metallic oxides, especially those of vanadium and molybdenum. It has been known for many years that vanadium oxide has the property of effecting oxidations of this character. In 1892, Walter[17] stated that in presence of air and vanadium oxide toluene could be converted into benzaldehyde or benzoic acid and anthracene into anthraquinone, and at a considerably later date (1904) he patented a number of catalysts suitable for this reaction. He also stated that, in addition to the above reactions, alcohol could be oxidised to aldehyde and acetic acid, benzene to diphenyl, naphthalene to β-naphthol, diphenylamine to carbazole, etc. Somewhat later, Woog[18] observed

the production of benzaldehyde from toluene in the presence of air at a platinum surface, and Loewenthal[19] obtained a patent in 1909 for the oxidation of aromatic hydrocarbons to aldehydes in presence of oxides of chromium; whilst Orloff,[20] whose work on the oxidation of methyl alcohol to formaldehyde at this period has already been discussed (p. 175), extended his investigations to certain hydrocarbon derivatives such as turpentine, heavy petroleum, benzene and toluene, obtaining benzaldehyde from the latter. During the war period H. D. Gibbs,[21] working on behalf of the American Government, studied the conversion of naphthalene into phthalic anhydride, indicating appropriate conditions of catalyst and temperature for obtaining commercial yields of the latter, and also of anthraquinone from anthracene, benzaldehyde from toluene, etc.

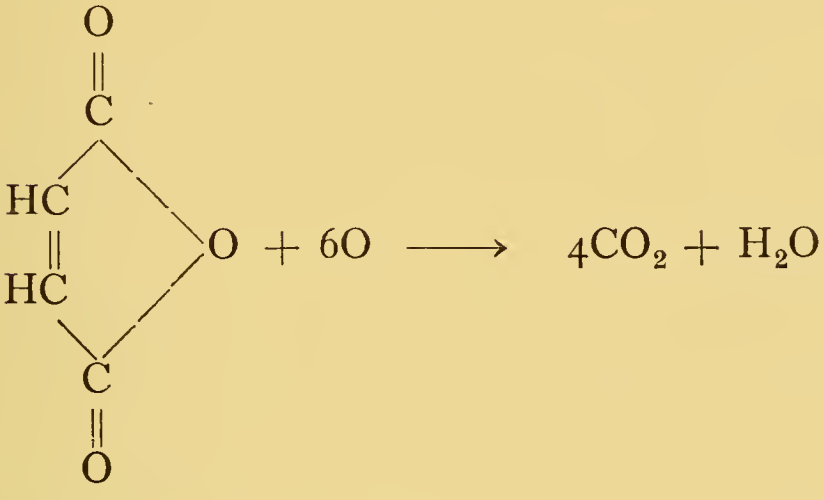
The most elaborate work in this field, however, appears to be that of Weiss and Downs,[22] and the Barrett Co. of New York. The main contribution which they have made to the solution of the problem is in controlling the temperature conditions so as to secure the minimum amount of destructive oxidation; further, they have paid more definite attention than previous investigators to the consecutive stages of the oxidation process in given cases. Thus, for example, they have shown that the oxidation of benzene proceeds in three definite stages, namely,



Benzene. Quinone.



Quinone. Maleic anhydride.



Maleic anhydride.

In the ordinary combustion of benzene it is probable, in fact almost certain, that these intermediate products are formed, but at the temperature of active combustion the speed of the final reaction is as great or greater than that of the intermediate phases. If, however, the amount of oxygen present with the benzene is suitably adjusted and reaction is made to take place at a relatively low temperature, for example, at 350°–450° at the surface of an appropriate material, the products depend largely on the nature of the latter substance. Weiss and Downs classify catalysts as " productive catalysts " and " active catalysts " ; the latter term refers to substances which substantially yield only completely oxidised products (they mention, for example, that whilst platinum is very highly active, it tends to produce the completely oxidised materials, *i.e.*, carbon dioxide and water). The " productive catalysts," on the other

hand, are those which under suitable conditions lead mainly to an intermediate stage, so that a relatively high yield of a desired intermediate oxidation product can be successfully isolated. The first step in the systematic investigation, therefore, was to select suitable " productive catalysts." Vanadium oxide appears at present to be the preferred material, with molybdenum oxide a good second. Subsequent stages in the working out of the process consisted in the elaboration of a laboratory apparatus, and finally a technical plant, in which the temperature conditions and the proportion of air to hydrocarbon vapour could be maintained so as to give maximum efficiency in the process. A description of the technical procedure recommended by Downs [22] in a recent paper (1926) will now be given.

The large-scale unit described by Weiss and Downs consists of a multiple form of the individual laboratory type of catalyst tube. The latter is a square $\frac{5}{8}$-inch steel tube sufficiently long to contain a layer of the catalyst, and also to allow for pre-heating of the entering gases. Thus the tube may be from 10 in.–1 ft. in length, and contain a layer of 4–5 in. of catalyst supported towards its lower end. Great stress is laid upon the necessity for avoiding any development of local high temperatures in the catalyst mass. The whole aim of the design of this apparatus is to secure rapid removal of heat as fast as it is developed by the oxidation process. To this end, the catalyst itself consists of granules of aluminium which are coated with vanadium oxide, whilst the space above the catalyst may also, if desired, be filled with untreated aluminium pellets in order to assist in the conduction of heat. Further, the temperature is regulated very skilfully by enclosing the catalyst tube in an ordinary cylindrical tube provided with a header pipe. This tube is filled with mercury to a level a little higher than that of the catalyst in the inner tube. To start the reaction, the mercury is boiled and a mixture

of, say, benzene and air in the correct proportions is passed downwards through the catalyst tube. As soon as oxidation sets in, the heat developed exothermally is in excess of that required to maintain the desired temperature at, say, 400°, but is rapidly conducted to the mercury and dissipated in boiling the latter, the vaporised mercury being again condensed in the upper part of the apparatus as it pre-heats the interacting benzene-air mixture. Removal of the heat of reaction in this way (as latent heat of evaporation of a liquid boiling at or near the desired temperature) guarantees that the catalyst tube will be surrounded by a heat-removing bath, the temperature of which is the same at all points. Hence each tube operates exactly like its companions, and the results in a single laboratory tube can be duplicated in a plant converter where there are, say, a thousand tubes. This method is therefore superior, in the case of an exothermal action, to supplying heat by means of a bath of lead or other high-boiling liquid.

The most recent form of plant converter for this oxidation process is described as consisting of a nest of many catalyst tubes of the above type, set into perforated plates and surrounded by the cylindrical jacket of the converter, the interstices between the tubes and the jacket being employed as the vapour bath consisting of mercury or, according to a later suggestion, of melted sulphur. In order to obtain the minimum volume of mercury or sulphur and also to obtain the maximum volume of catalyst, square tubes are employed to hold the catalyst; this has the further advantage that heat can be removed more efficiently since the ratio of tube surface to catalyst volume is much greater in a square tube than in a round tube. The cylindrical jacket enclosing the nest of tubes is connected to two or more pipes at its upper end, which act as reflux condensers for the mercury or sulphur vapour, and by means of which, if necessary, nitrogen can be admitted under pressure, so that, within limits, the boiling point of the bath can be raised to any desired temperature

above the normal boiling point of the liquid at atmospheric pressure. The hydrocarbon-air mixture enters at the top of the nest of catalysts, is pre-heated in the upper part of the latter, and passes over the catalyst in the lower part, the gaseous products of the reaction passing from the base of the vessel to fractional condensers, water scrubbers, etc., in which the products and unchanged raw material are separated and recovered. The losses of mercury or sulphur by vaporisation are exceedingly small, and hardly contribute anything appreciable to the running costs.

A converter of this type with outside dimensions 3 ft. in diameter by 4 ft. high, and containing a nest of $\frac{5}{8}$-in. square tubes spaced $\frac{3}{16}$ in. apart, will produce a ton of phthalic anhydride from naphthalene in twenty-four hours. The extent to which these processes are being developed in the United States can be gathered from the following quotations from the paper by Downs previously referred to :—

" Since the discovery by H. D. Gibbs of the vapour-phase catalytic production of phthalic anhydride from naphthalene in 1916, its production has expanded rapidly, until to-day it is being made in the United States at the rate of more than four million pounds per year. Most of this production is being consumed in the preparation of anthraquinone by condensing it with benzene in the presence of aluminium chloride and later treating the benzoylbenzoic acid thus formed with concentrated sulphuric acid. Anthraquinone made in this way is of a very high degree of purity. Methyl-anthraquinone and chloro-anthraquinone are similarly made. A yield of more than 80 lb. of phthalic anhydride per 100 lb. of naphthalene fed to the converter is obtained. By catalytic oxidation of toluene, benzaldehyde and benzoic acid free from chlorine can be made in a high state of purity.

" Anthraquinone can be made from crude anthracene. During its synthesis, the impurities such as phenanthrene and carbazole, are burned up. The production of anthraquinone by this process depends upon the economics of the process compared with its synthesis from phthalic anhydride. The cost of anthracene with no credit for the carbazole produced as a by-product is excessive in the United States, but the opportunities for the success of the process abroad are good.

" Maleic acid can be produced at a yield greater than 60 lb. per

100 lb. of benzene fed to the converter. The acid itself is not ordinarily recovered and sold as such, but is converted with theoretical yields into malic acid, by autoclaving in aqueous solution. Malic acid is a perfect substitute for citric acid, and in many respects is superior to tartaric acid as an organic acidulant. Other derivatives such as esters and condensation products heretofore unavailable can be made from maleic acid.

"Other hitherto rare compounds can be made from various aromatic substances. These have not as yet been placed on a manufacturing basis. The aliphatic compound field has been largely neglected."

From the general details given in the preceding paragraphs, it will be gathered that processes of controlled oxidation in the vapour phase at the surface of suitable catalysts should have a very important future in the manufacture of industrial organic chemicals. As in all other cases of industrial catalysis, the efficiency of the process depends entirely on the construction of large-scale converters, the design of which takes into account all the specific chemical factors of the particular operation. Thus, for example, Weiss and Downs find that in large-scale practice, correctly prepared forms of vanadium oxide possess a long life, acting satisfactorily for at least six months of continuous operation, during which time the amount of phthalic anhydride, for instance, produced is at least 20,000 times the weight of vanadium oxide present. The question of catalyst replenishment accordingly becomes of little practical importance; when at length it is desirable to replace a partially de-activated catalyst with a fresh charge, the vanadium oxide in the spent material is, of course, recovered by chemical means and the recovered vanadium solution employed in the production of new catalytic material.

It should be mentioned, in conclusion, that Maxted [23] has recently stated that tin vanadate is an effective catalyst in this process at 250°–300°, *i.e.*, at least 100° lower than the American catalyst.

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CHAPTER IX

HYDROGENATION OF LIQUID ORGANIC COMPOUNDS IN PRESENCE OF REDUCED METALS

NEARLY all organic compounds which contain ethylenic or acetylenic linkages, the benzenoid ring-system of many aromatic compounds, and many aldehydes or ketones undergo addition of hydrogen when treated in the liquid condition with gaseous hydrogen in presence of certain finely-divided reduced metals under appropriate conditions of temperature and pressure.

The metals in question include palladium, platinum, nickel, cobalt, and copper, but so far as industrial work is concerned, nickel is by far the most commonly employed, the noble metals being perhaps employed to a minor extent in the production of a few drugs and fine chemicals by hydrogenation.

The many potential applications of this method to industrial uses have, so far, been limited in practice to a very few instances by economic considerations: the hydrogenation or hardening of liquid fatty oils, the production of hydroaromatic derivatives from phenol, the cresols, and naphthalene, and the manufacture of a few isolated chemicals useful in pharmacy, perfumery, etc., of which the production of menthol from thymol or from piperitone may be given as an instance. Of these applications, the output of hydrogenated fats greatly exceeds the rest, in consequence of the wide scope for hardened fats in soaps, candles and also in edible products, and of the relatively low hydrogen consumption, much less hydrogen being required to produce an equal weight of finished product from fats than from phenol, naphthalene, or

other organic compound of comparatively small molecular size.

The Hydrogenation of Fats.[1]

Solid fats are of economic value as edible products, soaps, or candles, and the quantities required for these purposes are in the aggregate far greater than those of the liquid fats, or fatty oils, whose main outlets (in addition to soap) are for paints, lubricants, burning oils, leather-dressing, etc. Contrariwise, liquid fats preponderate in nature over those which are solid at ordinary temperatures, and the latter accordingly tend normally to be more valuable and possess a higher market value. Consequently it was attempted for many years to evolve a technical process for converting liquid into solid fats, or, as it was more usually termed, to transform oleic into stearic acid.

Broadly speaking, the main difference between solid and liquid natural fats or glycerides is the relative abundance in the latter of glycerol esters of the unsaturated oleic acid, or its still more unsaturated analogues, linoleic and linolenic acid :—

$CH_3.[CH_2]_7.CH : CH.[CH_2]_7.COOH$ Oleic acid.

$CH_3.[CH_2]_4.CH : CH.CH_2.CH : CH.[CH_2]_7.COOH$ Linoleic acid.

$CH_3.CH_2.CH : CH.CH_2.CH : CH.CH_2.CH : CH.[CH_2]_7.COOH$ Linolenic acid.

The natural fats of higher melting-point contain relatively more of the higher saturated acids (in combination with glycerol), for example :—

$CH_3.[CH_2]_{10}.COOH$	Lauric acid.
$CH_3.[CH_2]_{14}.COOH$	Palmitic acid.
$CH_3.[CH_2]_{16}.COOH$	Stearic acid.

Obviously reduction of (*i.e.*, addition of hydrogen to) glycerides of the former acids would furnish the corresponding derivatives of the solid stearic acid (m.p. 71°), and so numerous attempts, none of which

led to technical success, were made in the past fifty or eighty years to carry out the transformation of unsaturated into saturated acids. Thus it was proposed to heat oleic acid with phosphorus and iodine; or to fuse it with caustic potash, when palmitic acid is formed (this was actually put into practice by Radisson at Marseilles for some years); or to convert it into solid hydroxystearic acid and stearolactone by heating with zinc chloride (Benedikt) or with sulphuric acid (Geitel).

Sabatier,[2] however, in the course of his classical work on the catalytic hydrogenation of the vapours of organic compounds in presence of nickel, observed that oleic acid vapour was thus transformed into stearic acid; but he believed that hydrogenation only occurred in the state of vapour. Fokin also showed that oleic acid vapours were converted by hydrogen in presence of platinum into stearic acid.

The successful technical operation of a vapour hydrogenation process for oleic acid (b.pt. 290°/100 mm.) would be exceedingly difficult, whilst that of the non-volatile glycerides is of course out of the question; but, shortly after Sabatier's discovery, Normann[3] took out a patent in Germany in 1902 for the hydrogenation of unsaturated fats in the liquid state, and this process was the foundation of technical fat-hydrogenation. In the course of the next decade the observation of Normann was developed in several quarters into a process suitable for large-scale working, and by about 1910 the output of hydrogenated fats—chiefly hardened whale oil—probably amounted to several hundred tons per week. Since, at that period, the difference between the market prices of tallow and of whale and a few other liquid oils was about £15–£25 per ton, the process offered considerable attractions, and capacity was rapidly extended until, by the end of the war period of 1914–1918, the world's potential output of hardened fats had reached many thousands of tons per week. Several of the existing hydrogena-

tion plants in this country, on the Continent, and in America are each able to deal with as much as 1,000 tons of fat per week.

Since the war period, the demand for hardened fat has abated to some extent, the price of whale and other cheap oils having increased with the increased demand for these fats, whilst at the same time, and owing to a variety of causes, that of tallows has tended to decrease. The fat-hardening industry is, nevertheless, firmly established on a large scale ; on the one hand it serves to maintain a more even balance between the costs of soft and hard fats, and on the other it is safe to assert that, as time goes on and initial prejudices against the hardened products die away, the use of hydrogenated fats for specific ends, especially in edible fats, will increase rather than diminish.

Consideration of the theoretical side of industrial catalysis, which was dealt with in Section I, will cause the reader to appreciate that the work involved in developing fat-hydrogenation has contributed useful data in connection with the mechanism of heterogeneous catalytic actions ; it should also indicate the complexity of the practical issues which were faced by the pioneers of fat-hydrogenation at a time when theoretical knowledge of contact action was by no means so far advanced as at the present day. The practice of fat hardening is complicated further by the fact that, in addition to the actual hydrogenation process, the production of hydrogen of a definite standard of purity, the production of active catalyst and its recovery after use, and the removal of impurities from the oils treated have all to be carefully considered. A fat-hydrogenation plant is thus somewhat costly from the point of view of initial capital expenditure and the process tends to be concentrated in units of fairly large size, and, as a general rule, is conducted only by concerns of some magnitude.

In the actual hydrogenation, several types of

apparatus are in general use, and these may be classified broadly as follows :—

(i.) The *agitation system*, in which mechanical agitation is used to produce an intimate mixing of nickel, fatty acid and hydrogen ;

(ii.) The *circulation process*, in which a mixture of oil and catalyst is withdrawn from the lower part of the reaction vessel and injected as a fine spray into the gas-space at the top of the vessel by means of a pump ;

(iii.) The *continuous process*, in which oil passes downwards over a special type of stationary or massive catalyst and meets an upward current of hydrogen.

The details of the catalyst production and other features vary somewhat in these different systems, but in all cases the ancillary operations mentioned above have to be considered, and may be dealt with conveniently at this point before describing the actual hydrogenation process.

Hydrogen Production.

The amount of hydrogen fixed by different fats is, of course, dependent on their original state of unsaturation, and on whether they are to be converted into hard tallow-like fat, soft fat, or semi-liquid fatty oils. An average figure for hydrogen consumption over the usual range of oils dealt with in a fat-hardening installation is about 1 per cent. by weight of the fatty oil treated, or about 4,000 cub. ft. of hydrogen per ton of oil. It is not usually economical to conduct a hydrogenation plant on the agitation or circulation systems on an output of less than 200 tons per week, so that the minimum consumption of hydrogen is in the region of 800,000 cub. ft., and may be four or five times as much as this in a large plant. The amount of hydrogen required may thus be comparable with that of the coal-gas necessary for a large village or small town, and the production of hydrogen is, in itself, a modern industry of no mean size (*cf.* pp. 75, 104).

From the point of view of fat-hydrogenation, the following notes may be added here on hydrogen production.

Electrolytic hydrogen.—Hydrogen produced from water by electrolysis is by far the best for catalytic purposes, owing to the absence of any toxic compounds such as traces of sulphur derivatives or carbon monoxide; traces of oxygen, the only possible impurity, are no practical detriment in fat hydrogenation. The cost of production of electrolytic hydrogen in the absence of cheap (water-power) electricity makes its use impracticable in many centres of the fat industries, including England; the large fat-hardening installation of the De-No-Fa Company at Fredrikstad, in Norway is, however, fed by electrolytic hydrogen, and this source is also utilised in some factories in Italy and in Switzerland. Specially designed batteries of cells for the production of hydrogen are available for catalytic purposes, and in this connection the patented processes of Knowles [4] represent good modern practice.

Hydrogen by the Bergius Process.—Mention may be made of the process devised by Bergius [5] for the production of hydrogen by the direct action of liquid water on iron at high temperatures, although this method has not yet, to the writer's knowledge, found application on the large scale in England. The action is carried out in a vessel capable of withstanding pressures of the order of 500 atmospheres, and consists in charging the vessel with water and suitable iron scrap and heating it to about 300°–350°; preferably in presence of small amounts of ferrous salts and copper. At this temperature and the corresponding pressure (about 250–300 atmospheres) the action is very rapid, and it is said that as much as 3,000 cub. ft. of hydrogen per day can be obtained from a bomb of ten gallons capacity. The hydrogen is of very high purity and is of course available for use at these high pressures without mechanical compression—a factor which, however,

does not bear directly upon the case of fat-hardening. The action is simply the usual decomposition :

$$3Fe + 4H_2O = 4H_2 + Fe_3O_4,$$

and silicon, phosphorus or carbon compounds present in the metal remain for the most part unattacked.

Hydrogen from Water-gas.—Hydrogen may be separated from those constituents of water-gas (including carbon monoxide and dioxide), which are relatively liquefiable by passage through a Linde or other liquefaction plant, and it is produced technically by this means in some fat-hardening installations. The gas obtained is, however, by no means free from carbon monoxide.

Water-gas may also be converted into hydrogen by the catalytic process described in a previous chapter (p. 80). This method of manufacture gives a higher yield of hydrogen in proportion to the water-gas consumed than any other, and is widely employed in preparing hydrogen for the commercial synthesis of ammonia (p. 104). The crude hydrogen contains a certain small proportion of untransformed carbon monoxide, however, and this requires removal by compression, through ammoniacal copper solutions or otherwise, before the gas is strictly suitable for use in fat-hydrogenation.

The catalytic process summed up in the equation

$$CO + H_2O = CO_2 + H_2$$

may be regarded as the resultant of two simultaneous actions, *e.g.*,

$$CO + Fe_3O_4 = 3FeO + CO_2$$
$$3FeO + H_2O = Fe_3O_4 + H_2,$$

and earlier processes in which these actions were carried out consecutively instead of concurrently were developed for the production of commercial hydrogen for fat-hydrogenation and other purposes. Although these methods involve the consumption of somewhat more water-gas per unit of hydrogen than the catalytic

process, the crude hydrogen produced contains less impurity than in the latter case, and may reach a purity of well over 99 per cent. For this reason the processes in question are still in considerable favour with manufacturers of hardened fats, and some account of their operation should be included here.

The Lane Process.—This consists in the alternate reduction of iron-oxide ore by water-gas and passage of steam over the reduced oxide, which regenerates iron oxide and sets free hydrogen. In the form advocated in the patents of Lane,[6] the iron oxide, usually small fragments of hydrated spathic or bog iron ore, is packed into retorts about 8 in. in diameter and about 9 ft. in length, a number of these retorts being set horizontally in a brickwork furnace and heated by water-gas firing. The cycle of operations in the plant consists in reducing the ore by pre-heated water-gas for about 20 minutes, followed by a period of about 10 minutes, when superheated steam is passed over the reduced material. The spent water-gas from the reducing period passes to the heating flues and thence to waste, whilst the first portions of steam and hydrogen from the working period are also rejected in order to eliminate carbon monoxide as completely as possible. The hydrogen produced is passed to a gas-holder after purification, as described below. At its best this process should yield one volume of hydrogen for not more than two volumes of water-gas consumed in reducing the ore and supplying heat.

The Messerschmitt[7] *and Bamag*[8] *Processes.*—A modification of the intermittent iron water-gas process, devised by Messerschmitt[7] and others, has been much employed in Germany, and was adopted by the German authorities as the most efficient mode of producing hydrogen for airships. The retort batteries of the Lane system are replaced by a single vertical furnace of a kiln-like type (" Schachtofen "), which consists of a shaft of annular cross-section containing a large quantity of the broken iron ore with an internal

heating flue in the centre and other flues surrounding the shaft externally. The whole furnace is enclosed in firebrick. The cycle of operations is much the same as in the Lane process, and heat is applied by the flues, whilst the charge of ore may be increased in temperature intermittently by burning a mixture of water-gas and air within the furnace itself. It is claimed that this system is more economical to run than the Lane process, and that less water-gas is required to furnish a given value of hydrogen; the source of economy is mainly the heating system employed, which requires less fuel in the form of water-gas.

Hydrogen prepared by the Lane or Messerschmitt processes will contain only slight traces of sulphur compounds and about 0·2 per cent. at most of carbon monoxide.

Hydrogen Purification.

The last-mentioned compounds should be removed as completely as possible from hydrogen which is to be employed in fat-hydrogenation, and purification may be effected in the following ways :

(*a*) *Sulphur Compounds*.—These include sulphuretted hydrogen and volatile compounds containing sulphur and carbon, such as carbon disulphide and carbon oxysulphide, COS ; complete elimination of the latter substance offers considerable difficulty.

The crude hydrogen is usually first passed through a series of scrubbing boxes containing wet hydrated iron oxide, as in the case of water-gas or coal-gas, and this procedure effects fairly complete removal of free sulphuretted hydrogen, whilst some of the organic sulphur compounds are also trapped. To reduce the sulphur content of the gas to a minimum, however, it is necessary to submit the partially-cleansed hydrogen to further scrubbing, either by passage through slaked lime, or through a solution of caustic soda. The hydrogen should then be sufficiently free from sulphur compounds to be suitable for use.

(*b*) *Carbon Monoxide*.—This is still more difficult to eliminate completely, and it may be pointed out here that it is quite possible, and is indeed a frequent practice, to operate with hydrogen containing small proportions of this gas (*e.g.*, below 1 per cent.). The action of carbon monoxide as a catalyst " poison " is somewhat different from that of sulphur compounds. Sulphuretted hydrogen, for example, is exceedingly strongly adsorbed by nickel, and also tends to pass beyond the adsorption stage to direct chemical combination and production of nickel sulphide ; the adsorption by nickel of carbon monoxide, although very marked, is more comparable with that of the unsaturated organic compounds to be hydrogenated, and the main result of the presence of a reasonably small concentration of carbon monoxide is to slow down, rather than to suppress, hydrogenation of the fats. Moreover, the toxic effect of carbon monoxide declines considerably with increase of temperature, and the use of hydrogen containing this impurity can be compensated for to some extent by employing a higher working temperature.

Carbon monoxide may be eliminated, or reduced in quantity, in technical practice by one of three methods :

(*a*) The hydrogen may be passed under compression through a scrubber containing an ammoniacal solution of a copper salt, as in the Badische contact process (*cf.* p. 83).

(*b*) The hydrogen may be mixed with a small proportion (about 1 per cent.), of oxygen and passed at a temperature of about 100°–150° over mixed catalysts composed of the oxides of iron, copper or manganese. Under these conditions, as shown by Harger, Rideal, and others, the carbon monoxide is oxidised to some extent preferentially to the hydrogen, so that, although a small amount of hydrogen is also lost as water, the whole of the carbon monoxide is converted into inert carbon dioxide (*cf.* p. 173).

(*c*) By simple passage of the hydrogen over a nickel

catalyst at 250° or above, any carbon monoxide present is converted into methane by the original action of Sabatier and Senderens :—

$$CO + 3H_2 = CH_4 + H_2O$$

This method also completely removes the carbon monoxide, but leaves in its place a corresponding volume of methane, useless, although not toxic, as regards hydrogenation ; difficulties are also liable to be encountered in maintaining the nickel catalyst in a state of prolonged activity, since it tends to become fouled with accumulated impurities of various kinds abstracted from the large volumes of hydrogen passed over it, whilst the cost of heating the hydrogen to the necessary temperature is by no means negligible.

Purification of Fats prior to Hydrogenation.

It is also necessary that fats which are to undergo hydrogenation should be reasonably free from impurities prejudicial to the catalyst. In decreasing order of toxicity to catalytic nickel, the impurities likely to be present are organic sulphur compounds, oxidised unsaturated fatty compounds, whether degradation products (fatty acids of low molecular weight) or complex oxygen addition-products of a peroxidic or "linoxyn" type, colloidal suspensions of mucilage, protein, etc., moisture, and free higher fatty acids.

Free fatty acidity (up to about 3 per cent., and if the acids are those originally present as glyceride in the natural fat) does not hinder the course of hydrogenation to an uneconomic extent, and oils of this degree of acidity may be treated without preliminary neutralisation of the free acids.

Moisture is avoided as far as ordinary precautions may be taken, although it is unnecessary to attempt to maintain a rigidly anhydrous condition. The nickel, especially if supported on materials which are good adsorbents for water, tends to adsorb moisture preferentially to fat and, even at the temperature of reac-

tion, may retain an adsorbed film of water which hinders contact between liquid fat and the catalytic metal.

The other impurities mentioned are toxic even in small concentration, owing to their adsorption by the nickel in preference to that of the unsaturated fatty compounds.

Organic sulphur compounds are found but rarely in neutral fats, although sulphur may be present owing to the oils having been extracted by carbon disulphide ; it is not usually necessary, however, to employ oils extracted by this solvent for hydrogenation. Organic sulphur compounds are somewhat difficult to remove adequately in technical practice.

Oxidised glycerides and colloidal or other mucilage are generally removable by refining the fat either with aqueous caustic alkali or by agitation with a mineral earth or decolorising charcoal.

Catalyst Production.

For the purpose of general description it is sufficient to indicate the different forms of nickel which have been proposed for use in fat-hydrogenation—or rather, to make a judicious selection from the enormous variety of proposals existent in the patent literature of the subject.

The technical use of metals other than nickel in fat-hardening is confined practically to that of the rare metals palladium and platinum, which were formerly recommended on the score of relative activity and also because it was held that they could be employed at a substantially lower temperature than nickel. For technical purposes it is not practicable to use the delicate but unstable metal sols, which are effective at little above room-temperature, and so the palladium or platinum is supported on an inert material such as light magnesia.[9] In this condition the necessary temperature is appreciably higher than in the sol form, and the working temperature of nickel catalysts can, if neces-

sary, be reduced to much the same degree as that of the noble metals, of course with proportionate diminution in the rate of hydrogenation. This consideration, together with the fact that any greater activity possessed by palladium or platinum as compared with nickel is more than offset by the difference in cost of the metals, has led to the use of the rare metal hydrogenating catalysts being restricted to a few special cases, relatively insignificant in total output.

The form of nickel catalyst employed depends to a large extent on the actual procedure followed in hardening the fat—in the continuous method it is necessary to have a massive or granular form of catalyst, but in the other methods a more or less finely-divided substance is desirable. In either case it is of course essential to secure that a reasonable degree of activity is possessed by the catalyst and that the activity should not decline with undue rapidity, whilst in the case of powdered catalysts it is necessary to have these in a form which permits of complete and easy separation from the hardened fat by means of filtration.

The properties of activity and durability depend on the theoretical considerations which have been outlined in Section I. (pp. 22, 36), and notably upon the extent of catalytic surface available in conjunction with the state of the latter being as resistant as possible to the temperature conditions involved, and, to the extent to which control can be exerted, to the action of catalyst "poisons."

From the theoretical principles mentioned, it will be obvious that a smooth surface of metallic nickel, such as that of an electrolytically deposited film or smooth metal turnings, will possess quite negligible catalytic properties. On the other hand, Richardson [10] has shown that by sufficiently intense mechanical abrasion, nickel turnings can be made to acquire catalytic activity, the surface of the disintegrated metal becoming sufficiently "roughened" to produce

the irregular or exposed conformation of nickel atoms which apparently conditions catalytic power. Similarly, Bolton and Lush,[11] in their continuous hydrogenation process, use a catalyst in compact form which consists primarily of a mass of fine nickel turnings or nickel wool held in an openwork nickel frame. The surface of the nickel is rendered catalytic, either by immersing it as the anode in a dilute solution of sodium carbonate which is electrolysed at a suitable current density, or by steeping it in a bath of dilute sodium hypochlorite of definite concentration. The metal thus receives, by either process, a superficial coating of an adherent film of oxide which yields an active catalyst when, after washing and drying, it is replaced in the hydrogenation vessel and exposed to the action of hydrogen at about 250°.

In the discontinuous processes of fat hydrogenation the catalyst employed is usually finely-divided nickel prepared by controlled reduction of the precipitated hydroxide or carbonate. As pointed out by Sabatier, Kelber [12] and others, completely reduced nickel powder itself cannot be exposed to a temperature much above 300° without loss of activity, whereas certain supported nickel catalysts will withstand a temperature of 500°. This is what is to be expected, since the irregular or exposed particles of nickel atoms at the surface are known to collapse or contract together at temperatures far below the ordinary " sintering " temperature of the metal; the interposition of irreducible atoms or molecules amongst the atoms of nickel may be supposed to restrain the cohesive forces which are mutually exerted by adjacent atoms of the metal itself.

Hence it is usual to mount the nickel on a support such as kieselguhr or charcoal, powdered pumice, powdered asbestos, powdered porous firebrick, silica gels, or the like; this practice not only increases the power of resistance to high temperatures, but also yields materials which are much more readily filtered

and which can be washed with much greater ease prior to reduction.

Such catalysts are prepared by precipitating a boiling solution of, for example, nickel sulphate, in which the support is suspended, with a slight excess of sodium carbonate, and thoroughly washing the precipitated carbonate on the support or carrier in order to remove all soluble salts. When washing is complete, the material is dried until friable and then reduced in a current of hydrogen at a suitable temperature, which may be from 300°–500° according to the support used. Obviously the reduced catalyst must not be exposed to atmospheric oxygen sufficiently to involve loss of catalytic activity by surface oxidation.

If a granular support such as pumice or fireclay is employed, the resulting catalyst is suitable for continuous process work, but in practice the oxidised metal turnings referred to on p. 221 are more convenient.

In order to overcome the difficulty of handling reduced nickel catalyst in bulk, the reduction of suitable nickel compounds *in situ* beneath the oil which is to be hydrogenated, at about 250°, has been adopted in some factories. Bedford and Williams [13] recommended the reduction of nickel oxides, and Wimmer and Higgins [14] that of nickel formate in this manner, no support being necessarily employed.

Fat-Hydrogenation Plants.

(i.) *Agitation Systems.*—Different types of apparatus have been introduced by various designers, the essential principle in all of which is that hydrogen is admitted at the lower part of a vessel and rises through the body of mixed fatty oil and catalyst whilst the whole is kept thoroughly mixed by mechanical agitation. The stirring must be as thorough as possible, in order to provide rapid renewal of the liquid films at the surface

of the solid particles and to keep the latter evenly distributed throughout the body of the liquid. The fat is conveniently handled in units dealing with up to ten or twenty tons at a time ; the agitation is variously effected, either by a vertical rotating shaft carrying horizontal blades working against baffles,[15] a horizontal rotary stirrer of similar type, an inverted cone stirrer, a " Typhoon " type of stirrer, etc.

The vessel is usually cylindrical in section and fitted with closed coils, which serve either for supplying heat by steam or cooling with water. Hydrogen enters near the base and leaves at the top by an exit pipe connected with a safety valve. The concentration of nickel may vary according to circumstances from about 0·1–1 per cent. of the fat-charge, and the operation may be carried out between 120° and 200°, usually at a pressure of between 2 and 5 atmospheres of hydrogen.

The optimum temperature of hydrogenation of fats is about 170°–180°, and the action is strongly exothermic in character, so that moderation of the temperature by cooling may be necessary.

(ii.) *Circulatory Systems*.[16]—Here again, there are several variants of the main principle, which consists in circulating the oil and catalyst through an atmosphere of hydrogen, instead of passing the latter through the liquid. The hydrogen is admitted through the lid of the vessel, fresh gas entering only to replace that which is combined chemically with the fat. From the lower part of the vessel a pipe communicates with a pump which continuously removes oil and catalyst, and delivers the mixture through a further pipe passing into the vessel near the top, and terminating in a spray nozzle directed towards the inside of the lid.

The proportion of the catalyst is preferably kept as low as possible (*e.g.*, 0·1–0·3 per cent. of nickel) in order to facilitate the circulation, the temperature is raised to about 170°–200° and, the gas-space having

been completely filled with hydrogen, the charge is circulated until hydrogenation has reached the desired point. The process is usually conducted under considerably higher pressures than in the agitation systems, for example, from about 8–12 atmospheres.

This method avoids the difficulties inherent at the gland of a moving-shaft, which are somewhat troublesome when dealing with oil and hydrogen at a high temperature, but necessitates the use of a closed gas system ; this involves the steady accumulation of gaseous impurities, whether toxic to the catalyst or merely inert diluents. The process is thus best adapted for work with very pure gas, such as electrolytic hydrogen.

(iii.) *Continuous System*.[17]—The oil to be hydrogenated is admitted at the top of the closed hydrogenation vessel, and trickles down over nickel catalyst consisting of turnings activated as described above (p. 221), whilst it meets a current of hydrogen passing up through the vessel. Excess of hydrogen is collected from the top of the vessel, and hydrogenated fat collects at the bottom and is continuously removed by a seal pipe.

Whilst this process entered the field considerably later than the others, it appears to offer several advantages over the earlier methods, providing that the preparation, regeneration and efficiency of the stationary catalyst are technically satisfactory.

Separation of Catalyst from the Hydrogenated Fat.—In the continuous system the fat will not, as a rule, carry away with it more than traces of nickel. In the other processes the catalyst is readily removed by passing the hardened fat, whilst still warm and liquid, through a filter-press. The residual catalyst usually retains appreciable quantities of fat and, unless it is to be again employed in hardening a further batch or batches of oil, it may be extracted with benzine or similar solvent in order to recover the entrained fat.

From a deactivated or spent catalyst the nickel may be recovered, after removal of the fat as described, by solution in mineral acid ; it is then available for use in the preparation of fresh catalyst, so that, apart from small mechanical losses, the nickel in process may be regarded as a capital charge.

Properties of Hydrogenated Fats and the Course of the Hydrogenation Action.

The fatty oils differ widely in composition, and consequently the composition and properties of the hydrogenated products vary to a considerable extent. A detailed account of the products to be obtained cannot be given here, but will be found in volumes dealing with the fat industries. Some indication of the variations in question may be afforded by a comparison of the melting-points of the following oils when completely hydrogenated :—

Completely Hydrogenated.	M.p.
Coconut, palm kernel oils .	43°–45°
Fish oils, whale oil . .	52°–56°
Cotton-seed oil . . .	62°–63°
Olive oil, arachis oils . .	68°–69°
Soya bean, linseed oils . .	69°–71°
Castor oil	86°–90°

For technical purposes, *e.g.*, in the edible fat, soap or candle trades, complete saturation is rarely desired, and the progress of hydrogenation is followed by determination of the setting-point or iodine absorption on small test samples, or more rapidly by determining the refractive index of the fat, which falls parallel with the degree of saturation.

For the oils chiefly used in hydrogenation (whale, fish, linseed, soya-bean and cotton-seed oils), the consistency and melting-points of the hardened fats are

approximately related to their degree of unsaturation (iodine absorption) as follows :—

Iodine Absorption of Hardened Oils.	Consistency.
80–90	Semi-liquid thin pastes.
65–80	Soft pastes, m.p. 30°–35°.
50–65	Soft tallows, m.p. 35°–45°.
35–50	Hard tallows, m.p. 45°–52°.
–35	Very hard tallows, m.p. 52°–55°.

Two factors connected with the course of fat-hydrogenation should be briefly mentioned :—

(i.) *Selective Hydrogenation.*—If a mixture of olein with more unsaturated glycerides such as linolein, is hydrogenated, the latter is practically entirely transformed into olein before any of this is converted, in turn, into stearin (*cf.* p. 19). Thus the olein has to wait its turn, and, in a very rough manner of speaking, it may be said that, during hydrogenation, all the highly unsaturated fats pass through a stage corresponding to that of olive oil before they proceed to complete saturation.

Two important consequences follow from the selective character of the process :—

(*a*) Except over a very limited range, the composition of a hardened fat of given iodine number (say 50) cannot be simulated by mixing a much less hardened with a much more hardened fat (*e.g.*, one of 90 with one of 10 iodine number). The composition of the mixture will not be the same as that of the straight hardened fat.

(*b*) The olein type of glyceride is a most suitable material for many purposes, such as soaps, and for edible fats (in which any tendency to rancidity is a serious objection). Unfortunately the story is not so simple as it appears, because there is not one, but a number of " oleins " or glycerides of different mono-

ethylenic acids to be met with in hydrogenated fats, and not all of these are equally suitable for industrial use.

(ii.) *Isomeric Changes During Hydrogenation.*—In a highly unsaturated glyceride, the ethylenic linkages occur at different points along the chain of carbon atoms, and so a number of isomeric "oleins" usually result, some of which are glycerides of oleic acids which are isomeric with the ordinary oleic acid of nature, but which differ from the latter in being solid at the ordinary temperature.

Again, when the glyceride of natural liquid oleic acid is hydrogenated, isomerisation as well as saturation takes place (*cf.* Section I., p. 18) and the corresponding glycerides of elaidic acid and of other solid iso-oleic acids are produced.

The iso-oleins are objectionable in practice, not because of their higher melting-point, but for the following reasons :—

(*a*) The soaps of the solid oleic acids are less soluble and much less free in lathering power than sodium oleate ;

(*b*) The crystal structure of the solid iso-oleins differs from that of the saturated glycerides and tends to affect the consistency and appearance of edible fats in which they are present ;

(*c*) The crystal structures of the corresponding free iso-oleic acids are less tractable than those of palmitic and stearic acids, which are the acids normally present in candle-making material.

These difficulties are the only serious obstacles to the complete replacement, if necessary, of natural solid fats by the hydrogenated products, and they can be overcome to a large extent by suitable adjustment of the fat-charges employed in the various industries. At present fat hydrogenation is capable of controlling the price and output of the harder natural fats to a very marked degree, and in due course it is to be anticipated that many specific products of useful properties will be

developed from the enormous range of semi-synthetic glyceride mixtures potentially available in hardened fats from different sources.

Prejudices which have been manifested against the use of hardened fats in edible fats, soaps, etc., will die out in due course. Except for absence of vitamins, it is established that they are in every sense hygienic and nutritious ; they are usually superior in colour, either as fat or soap, to most natural fats ; and, whilst objection could at one time be taken to a specific odour associated with soaps or fats containing hydrogenated material, it is reasonable to say that with due precaution in the hydrogenation treatment the products are almost odourless, or at most possess a very faint, not unpleasant, characteristic odour.

Hydrogenation of Benzenoid Compounds.

Liquid hydrogenation has been applied on a commercial scale to a few compounds of the benzene series, notably phenols and naphthalene. The extent of this industry does not compare with that of fat hardening, although it is growing in importance ; it is, and probably will remain, more comparable with that of fine chemicals or organic " intermediates " as regards extent of output. A not unimportant factor in commercial hydrogenation of the aromatic nucleus is the consumption of hydrogen : whereas the average volume of hydrogen required per ton of fatty oil is of the order of 4,000 cubic feet, the production of one ton of cyclohexanol from phenol requires nearly 25,000 cubic feet, and that of one ton of tetrahydronaphthalene from naphthalene 12,000 cubic feet of hydrogen.

The first patents which drew general attention to the possibility of employing hydrogenation for other compounds than the fats in the liquid state were those of Brochet,[18] although Ipatiew's somewhat earlier publications[19], dealing with hydrogenations at what were then enormous pressures (100–150 atmospheres),

pointed to the general feasibility of the process. Brochet's claims included the hydrogenation of phenols, indigo and other materials of a like character, and in general he advocated the use of about 1 per cent. of nickel at a relatively low temperature (100°–120°), and a moderately high pressure (10–15 atmospheres).

Later work has established to a certain extent specific conditions of treatment for the technical manipulation of different types of compound, and it must suffice here to give some account, by way of example, of the commercial production of cyclohexanols, hydronaphthalenes and menthol.

Hydrogenation of Phenols.—The commercial exploitation of reduced phenol and cresols originated in Germany under the stimulus of war conditions. The respective products from phenol and from cresols, first put on the market as hexalin and methylhexalin respectively, were found to form good emulsions with fatty soaps and to render the latter capable of holding a considerable percentage of hydrocarbon oil or tetrahydronaphthalene in homogeneous emulsion; the mixtures were found to be fairly firm in texture and their lathering power was improved rather than deteriorated. Such soaps are probably tending to replace the older naphtha or paraffin soaps.

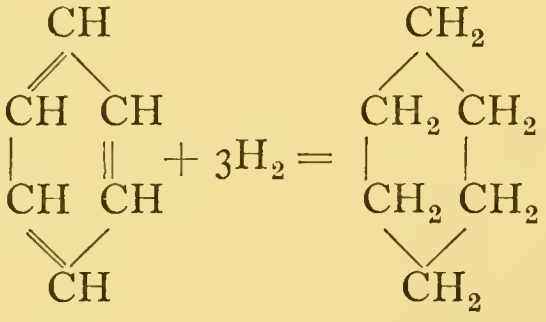
Hexalin and methylhexalin are also useful as solvents; they have a pleasing odour, somewhat camphoraceous in type, and the odour of their esters (for example, the acetates, which also possess good solvent properties), points to some of the latter class finding application in perfumery. It may be added that a British firm markets these products under the names of sextol (cyclohexanol), sextone (cyclohexanone), etc.

The manufacture of hydrogenated phenols may be conducted on the following general lines :—

The raw material must be freed from traces of thiocompounds and also from tarry matter, preferably by distillation in presence of a little caustic alkali. It is

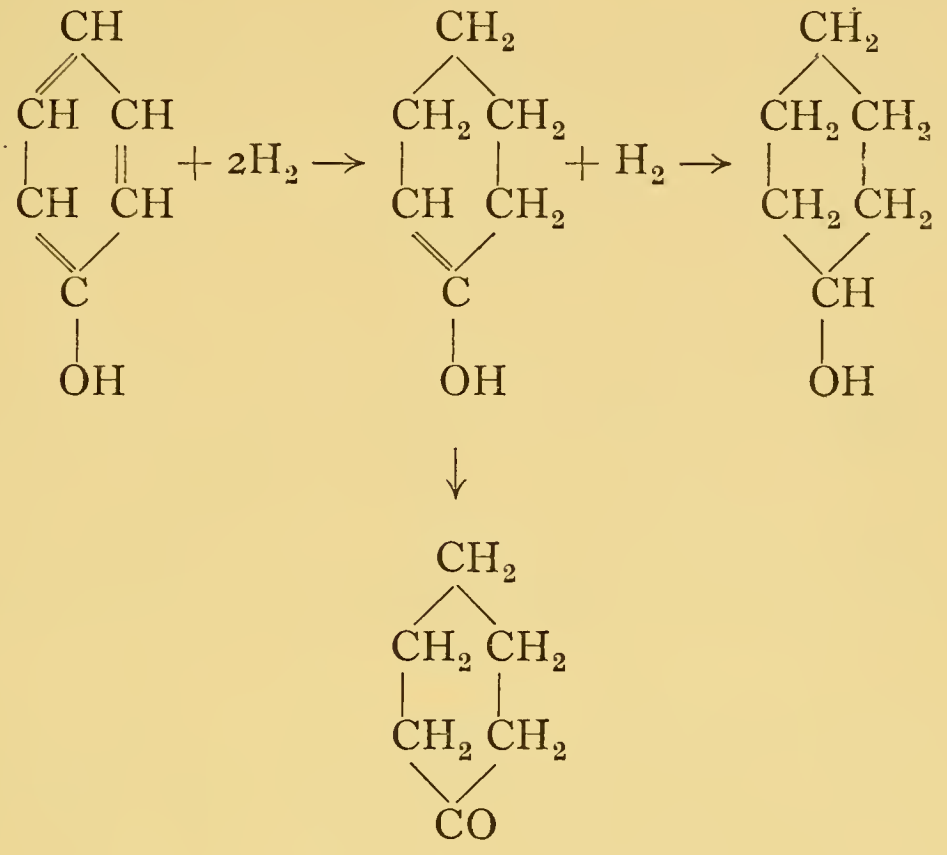
then placed in an apparatus of the agitation or circulatory types, together with a moderately high concentration (*e.g.*, 1 per cent. Ni) of active, and preferably supported, nickel catalyst ; a carefully controlled proportion of an anhydrous mildly alkaline salt (sodium carbonate in amount equal to 25 per cent. of the metallic nickel present) may be added with advantage as a "promoter." [20] The reduction proceeds rapidly at 160°–200°, whilst the pressure employed may be from 4 atmospheres upwards. Obviously, the higher the working pressure the smaller will be the escape of phenol or hydrogenated phenol vapours by evaporation, but apart from this it appears that a minimum, or "threshold," pressure is necessary before catalytic reduction of the benzenoid nucleus proceeds rapidly in the liquid state.

Hydrogenation should be complete in from one to four hours, and the products may be recovered either by filtration, or by distillation from the reduction vessel, leaving the catalyst, if sufficiently active, ready for a further charge. In addition to a little unchanged phenol, the product will contain a small proportion of tetrahydrophenol or cyclohexanone derivative ; the benzene ring system behaves as an individual unsaturated system during hydrogenation and, commencing with benzene itself, no dihydro- or tetrahydro-benzene is produced, but only cyclohexane :—



In the case of phenols, the action is similar, but addition of two molecules of hydrogen per molecule of phenol yields the enolic form of a cyclohexanone, and whilst this is mainly reduced further to a cyclohexanol,

some of it remains unchanged as the ketonic compound :—

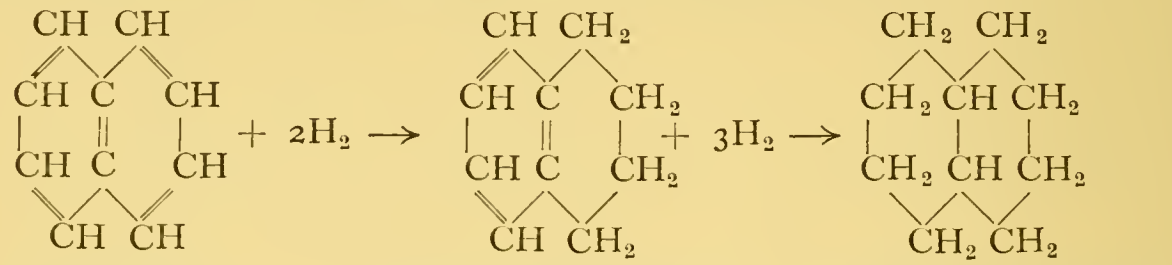


In the case of substituted phenols, two geometrically isomeric forms of the products are possible, and both are found in the hydrogenated material.

Whereas phenol melts at 43° and boils at 181°, the respective constants for cyclohexanol (hexahydrophenol) are 25° and 161°, and cyclohexanone boils at 166°. The six isomeric methylcyclohexanols and methylcyclohexanones are all liquids with somewhat higher boiling-points than those of cyclohexanol or cyclohexanone.

Hydrogenation of Naphthalene.—This has also been carried out on a fairly large scale, especially in Germany by Schroeter and the Tetralingesellschaft. The process is somewhat more difficult than in the case of phenols, because the purification of the raw naphthalene from thio-compounds demands considerable care and also because naphthalene appears to require a greater " threshold " pressure of hydrogen in order that addition of hydrogen may take place.

Reduction takes place in two stages as follows :—



Naphthalene. Tetrahydronaphthalene (Tetralin) ; b.pt. 206°–208°. Decahydronaphthalene (Dekalin), b.pt. 190°–191°.

Tetralin is a colourless liquid with a not unpleasant odour, and is a good solvent for many types of compounds. It is used to a notable extent as a thinner in paints and varnishes, in which it is stated to replace turpentine satisfactorily, whilst it is also serviceable as a fuel for internal combustion engines where economic considerations permit.

Dekalin, the fully hydrogenated naphthalene, has similar properties to tetralin, but the commercial hydrogenation is rarely carried to completion, since the extra consumption of hydrogen does not confer corresponding increase in the value of the product. The hydrogenated naphthalene on the market is frequently, however, a mixture of the two products in which the tetrahydro-derivative largely predominates.

The earlier patents and publications of Schroeter [21] and the Tetralingesellschaft [22] indicated that in order to obtain satisfactory hydrogenation it was desirable to refine the naphthalene by distillation over sodium, or better, by passing the naphthalene vapour through molten sodium. More recently it appears that sufficient purification results when the naphthalene is agitated with suitable qualities of fuller's earth, charcoal or kieselguhr, especially if the purified naphthalene is agitated subsequently with nickel catalyst and distilled from this into the hydrogenation vessel, which contains active catalyst suspended in tetrahydronaphthalene.

The hydrogenation may be effected in an agitator working at about 170°–200°, under a pressure of about

10–15 atmospheres ; one type of apparatus described in the literature, however, avoids the use of a mechanical stirrer, and consists of an autoclave which contains an unusually high charge of nickel on a porous or granular support. The apparatus is evacuated and a charge of purified naphthalene condensed into it after distillation from catalytic nickel, as mentioned. Hydrogen is then supplied at a pressure of 50 atmospheres or more, whilst the temperature is raised to about 170°, and absorption of the gas proceeds rapidly without stirring ; when the material has been completely converted into tetrahydronaphthalene (with a minor proportion of decahydronaphthalene), the pressure is reduced to below atmospheric, and the products are distilled under vacuum and condensed.

Without exposing the contents of the hydrogenator to air, a fresh charge of purified naphthalene is distilled into the vessel and hydrogenated by means of the same catalyst, until after a number of periods of use its activity declines beyond an effective point. It has been stated that by this means the same batch of catalyst may be used for as many as 100 consecutive hydrogenations.

Hydrogenation of other Aromatic or Terpene Derivatives.

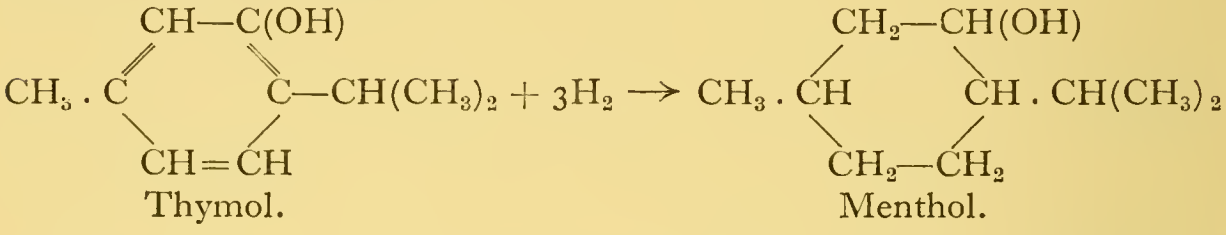
A certain number of perfumes or flavouring materials can be prepared by hydrogenation in the liquid state. Most of the unsaturated terpenes pass into saturated derivatives by this method, and in many cases the process is strongly selective, a diethylenic terpene yielding a monoethylenic compound (and frequently one only of two or more possible alternative isomerides) before any saturated derivative is produced. Relatively few of the products so far produced in the laboratory by these methods have any present value in commerce, but there is obviously considerable scope for technical research on these lines. The number of available raw materials is considerable, especially when it is remembered that aldehydic or ketonic radicles, which are also

frequently present in the natural compounds, are usually reducible to alcohols by the hydrogenation process.

One instance only will be quoted here as an example of this application of liquid hydrogenation—the production of synthetic menthol.

This has been effected in two ways :—

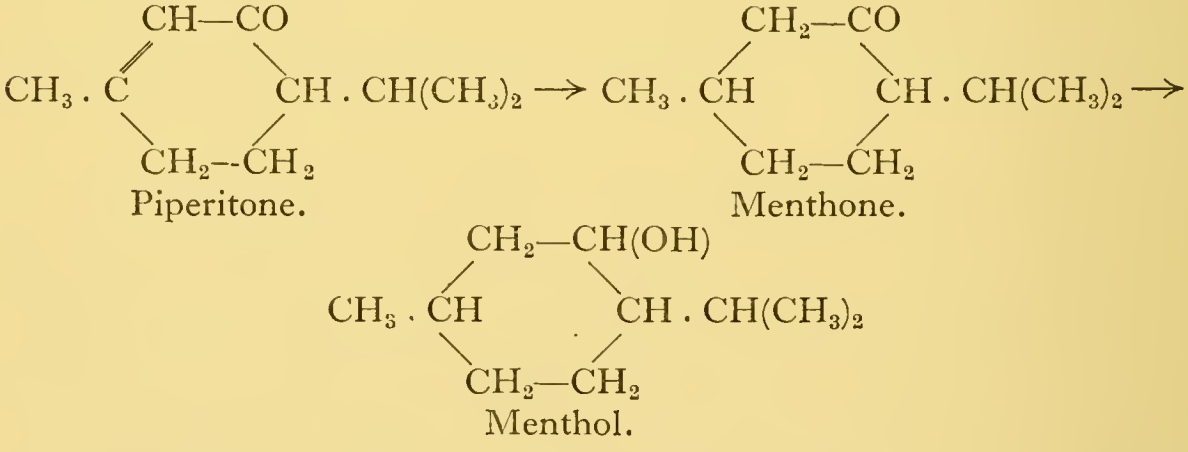
(*a*) From thymol by hydrogenation in a similar manner to that described in the case of other phenols (p. 229); this means has been employed to a certain extent in America :—



Thymol. Menthol.

(*b*) From the terpene ketone piperitone, which is found abundantly in certain classes of the Australian eucalyptus (especially *E. dives* and *E. piperita*).

The course of the action in this case may be represented as follows :—



Piperitone. Menthone. Menthol.

The hydrogenation proceeds readily at 150°–180° in presence of nickel under mild pressures of hydrogen (*e.g.*, 3–5 atmospheres).

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CHAPTER X

THE USE OF ACTIVATED CHARCOAL AS A CATALYST

THE element carbon, when in a form in which its surface is very large in comparison with the total volume present, has the properties of a catalyst in a number of reactions, and it is probable that its applications in this direction have not been yet by any means completely explored. A distinction must be drawn in the first place between forms of charcoal which are mainly useful for decolorising purposes (in which case the essential process is mainly adsorption of compounds of relatively high molecular weight at the surface or in the capillary interstices of a porous mass of charcoal) and carbons which, whilst as a rule highly efficient decolorising agents, also possess the property of catalysing certain reactions.

For example, animal charcoal, which consists essentially of a deposit of incinerated carbon on a mass of more or less porous calcium phosphate and other inorganic salts, has considerable decolorising power (although this is of a low order compared with modern types of absorbent carbon). Nevertheless, in certain industries, especially sugar refining, in which it is desired at the same time to remove soluble inorganic salts, animal charcoal is still preferred because the soluble mineral salts are removed or transposed at the same time by the action of the calcium salts present in the charcoal.

Modern charcoals, many of which are known in commerce under specific trade names, are produced by processes which employ, as a rule, one or other of the following general principles :—

(*a*) The destructive distillation of a specific wood

fibre followed by an oxygen-activation treatment of the product ;

(*b*) Destructive distillation of sawdust, etc., from selected sources, the sawdust being first impregnated with a solution of calcium chloride or a similar salt.

In the latter case, the distillation is carried on at about 800°–900° for about twenty-four hours until volatile matter ceases to come away. The products are discharged into water whilst hot, and thoroughly lixiviated first with boiling water and then with hot aqueous mineral acid, and finally again with water ; the washed charcoal is dried and ground mechanically to a suitable size. Apparently the thermal decomposition of carbohydrate matter so as to produce pure carbon is an extremely difficult process. In this distillation method, in which relatively little free oxygen is available, the decompositions involved are mainly those of elimination of water and condensation of the cellulose decomposition products with the production of more and more complicated forms, eventually, of difficultly volatile hydrocarbons. The final product from this process is therefore, in all probability, an extremely porous material with capillary interstices approaching molecular size, but the surface of the charcoal is not exclusively elemental carbon, but contains appreciable amounts of films of hydrocarbons of very high molecular weight and low hydrogen content. Such charcoals are frequently highly active as adsorbent materials (that is, for decolorising and bleaching), but, according to Chaney [1] and other authorities, are not so useful as catalysts as that prepared by method (*a*).

The alternative procedure (*a*), which embodies an oxygen-activation treatment of the charcoal, consists in carbonising the wood fibre in retorts at about 700° until as much volatile matter as possible has been driven off. The temperature is then increased to 800°–900°, and the charcoal exposed to a current of steam or of air (or preferably, a mixture of the two,

for example, the charcoal may be heated at 800°–900° for a few hours in a current of pre-heated steam containing about 2–10 per cent. of air). The surface films of complex hydrocarbons are removed by the controlled oxidation process and, moreover, the elemental carbon surface is doubtless also partially attacked so that, in addition to the porous structure of the whole mass, the carbon walls enclosing the capillaries consist not of a smooth surface, but of what may be regarded as a lattice work of carbon atoms from which a number of the original atoms have been removed by oxidation ; the carbon surface is therefore of the type which, as has been shown in Section I., p. 21, is that characteristic of an active catalyst.

The correctness of this explanation is borne out by the work of Garner and Blench [2] on the heat of adsorption of oxygen by active charcoal surfaces of this nature. It was found that the values observed were far greater than any due merely to physical condensation of the gases in the capillaries of the charcoal, and that they were intermediate between the latter values and the heat of combustion of carbon in oxygen. The order of magnitude of the thermal adsorption effects is thus quite parallel with that of a mild chemical reaction and with those observed by H. S. Taylor and co-investigators in the case of nickel or copper and hydrogen, ethylene, carbon monoxide, etc.

A recent patent [3] describes the similar manufacture of active carbon from incinerated soda-cellulose black liquor.

The main applications of carbon as a catalyst include many cases of chlorination, for example, various bleaching processes in which chlorine (or a mixture of chlorine and air) is passed upwards through a tower containing the active carbon in granular form, down which the liquid undergoing treatment is allowed to pass. This procedure may be applied also to the

oxidation of unsaturated fatty oils of a drying nature by air, and to the sterilisation of water by chlorine, although in the latter case it is more usual to inject chlorine direct into reservoirs in which the water is stored. Active carbon is also effective in oxidising hydrogen sulphide or hydrogen phosphide in presence of small quantities of air, and is used to some extent in removing these impurities from industrial gases such as ammonia or acetylene.[4] It has also been proposed to employ active charcoal in the nitric acid absorption towers dealing with the gases from the catalytic oxidation of ammonia (*cf.* this Section, Chapter IV, p. 129); the rate of oxidation of the nitric oxide to nitrogen peroxides is stated to be increased 500 times by means of active charcoal, offering possibilities of considerable reduction in the adsorption tower space compared with existing systems.[5]

Of course, in a number of other cases, the surface condition of the activated charcoal is taken advantage of in its use as a support for other catalysts. In such cases the catalytic action of the charcoal itself does not, as a general rule, come into play, and the latter simply serves as a very efficient mechanical support for the specific catalyst which is necessary in the particular case. For example, nickel, platinum, palladium or copper may be deposited upon active charcoal, and the products are exceedingly active hydrogenating catalysts; such materials are not used to any great extent in industry simply because the cost of activated carbon is at present sufficiently high to restrict its application merely as a catalyst support, for many other cheaper forms of porous support yield catalysts of quite sufficient technical activity.

A few details may be given of specific applications of carbon as a catalyst in the production of one or two definite chemical products.

The most important material in the production of which active carbon plays some part at present is probably hydrochloric acid,[6] as a by-product from

the electrolytic soda industry. The case of hydrochloric acid is of general interest because it is a good illustration of the fluctuations in general method which take place in consequence of changing economic factors and general changes in technical procedure. Originally, hydrochloric acid was a by-product of the first phase of the Leblanc soda process, and was utilised in part as a raw material for chlorine and bleaching powder ; at the present time, although the salt-cake process is still used (mainly in conjunction with glass manufacture), increasing amounts of hydrochloric acid are produced from chlorine, instead of the reverse operation, for the by-products of the electrolytic soda industry consist of hydrogen and chlorine.

These gases can be combined directly by burning a jet of hydrogen in an atmosphere of chlorine, but this has been found to be a somewhat dangerous process on the large scale, and at times to give rise to explosion. The dangerous nature of the combustion is reduced to a large extent if chlorine is burnt in an atmosphere of hydrogen, but a still safer and equally effective method is to pass the mixed gases through a bed of granulated active charcoal set in a water-jacketed vessel, the temperature of the contact mass being kept below a certain limit by regulating the flow of water.

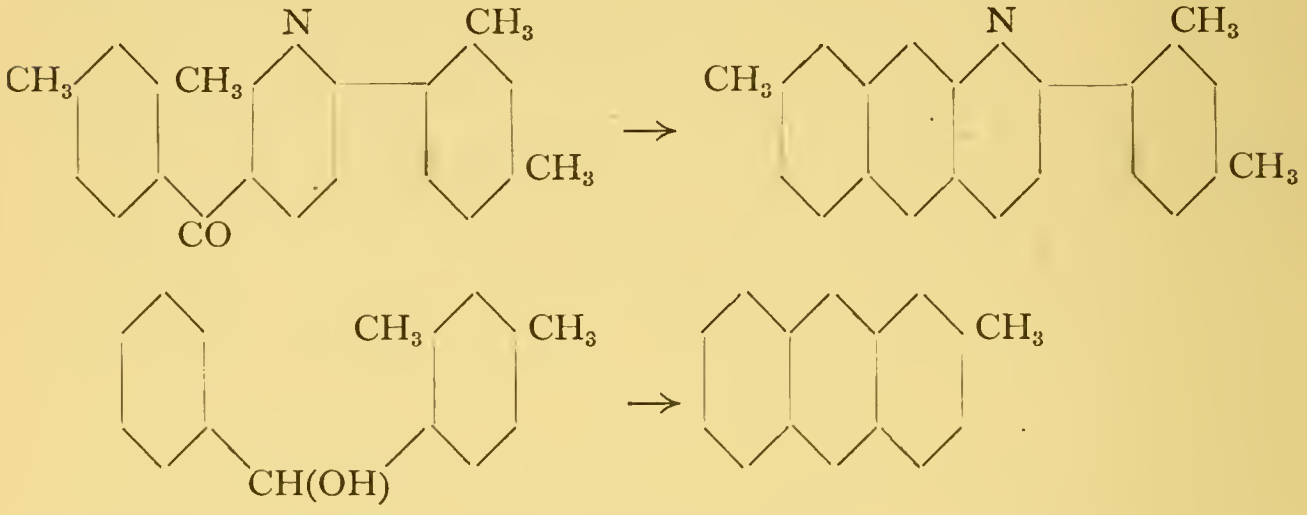
Another important industrial material produced by the intervention of active charcoal is carbonyl chloride or phosgene,[7] employed largely in the synthetic organic industry and also in chemical warfare, and to some extent as an insecticide, etc. The material was originally produced by exposing equal volumes of carbon monoxide and chlorine to bright sunlight or to ultra-violet rays, but it has been found to take place quite readily in the absence of light if the mixture of gases is passed through layers of activated charcoal at a moderate temperature, for example, about 100° –125°, and not above 150°. Probably all the phosgene manufactured at the present day is produced by the employment of carbon as a catalyst.

Activated charcoal has also lately been employed in the similar combination of sulphur dioxide and chlorine,[8] producing sulphuryl chloride, SO_2Cl_2, another substance of importance in the synthetic organic chemical industry. In this case the original procedure of passing mixtures of the gases over active charcoal appears to have been abandoned in favour of carrying out the combination in the liquid phase by suspending active charcoal in liquid sulphuryl chloride, and passing equal volumes of sulphur dioxide and chlorine into the solution. When the concentration of the catalyst falls below a certain point owing to the accumulation of sulphuryl chloride, the catalyst is separated by filtration and used again with a fresh, smaller proportion of sulphuryl chloride; the most active forms of carbon are capable of producing nearly 250 times their own weight of sulphuryl chloride per hour.

It is probable that active carbon could also be used with good effect as a chlorination catalyst in the case of many aromatic and other derivatives, in controlling the extent and yield of a desired product, but this does not appear yet to have been systematically studied; the suggestion has, however, been made, to produce hexachlorethane from ethyl chloride by this means.[9]

Finally, reference may be made to various recent processes which have been patented for the action of active charcoal on various types of exclusively organic chemical changes.[10] Thus, it has been stated that at 300°–350° active carbon converts unsaturated into saturated compounds in presence of steam, although from the details given (for example, the yield of stearic from oleic acid) it does not seem that the hydrogenating action is very vigorous. Other claims are for the use of active carbon in converting specific hydroxylic or ketonic aromatic compounds into polycyclic derivatives of the anthracene or quinoline types; the vapours of suitable compounds are passed, usually in presence of

a certain amount of air, over active carbon at about 400°, when actions such as the following are stated to occur :



Active carbon is also said to be a catalyst for the production of hydrogen from carbon monoxide and steam, of hydrobromic acid from bromine vapour and steam, and of methyl alcohol from carbon monoxide and hydrogen.

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SECTION III

CATALYSIS AT SURFACES OF COLLOIDAL ORGANIC COMPOUNDS (FERMENTATION PROCESSES)

SUFFICIENT has been said in Section I., Chapters I and III, to indicate the reasons for the inclusion of some account of fermentation processes in the present book. It is, of course, out of the question to deal fully with the many ramifications of the industries connected with the production of beer, wines and spirits, although the output of alcohol in these forms is doubtless far greater than that of the whole of the other fermentation products which will be mentioned.

From the catalytic standpoint the chief interest in technical fermentation processes is their adaptation to yield specific chemical products, and discussion will be confined for the most part to such cases.

The essential difference between fermentation catalysis and ordinary catalytic action has already been defined in Section I. as the employment of a catalyst (enzyme), which is produced by a living organism, and therefore the equipment of the technologist in these industries must include not only adequate knowledge of general catalysis and of chemical transformations, but also that of mycology, bacteriology, etc. A. Chaston Chapman,[1] in 1919, drew attention to the fact that "as a branch of chemical industry, industrial microbiology has not received in this country the amount of attention to which its importance entitles it"; in the nine years which have since elapsed it cannot be claimed that a great deal has been done to remedy this defect, other than the establishment of one or two important centres of research on industrial fermentation processes. Still less is there any sign of approximation to the ideal of Meldola[2] that: "when we can transform sugar

into alcohol in the laboratory at ordinary temperatures by the action of a synthesised nitrogenous organic compound ; when we can convert glucose into citric acid in the same way that *Citromyces* can effect this transformation ; when we can build up heptane, or cymene, or styrene, or when we can produce the naphthalene or anthracene complex in the laboratory by the interaction of organic compounds at ordinary temperatures, then may the chemist proclaim with confidence that there is no longer any mystery in vital chemistry." Nevertheless, in recent years, efficient processes for the production of glycerol, butyl alcohol and acetone from carbohydrates have been developed, and it would appear that the manufacture of lactic, citric and butyric acids from similar sources is on the eve of more scientific and efficient treatment.

Much further work is desirable on the isolation and study of specific organisms which will either give rise to higher yields than the cultures at present used, or on the other hand will lead to the production of other useful industrial chemical products. Such biochemical processes are likely to prove increasingly valuable by reducing or eliminating operating costs for fuel, power, and accessory chemicals, so long as the recovery of the products from the fermented liquor is not unduly difficult and expensive.

The examples to be dealt with in the present section include the alcoholic fermentation of sugars, mainly with reference to the variant which leads to the production of comparatively high proportions of glycerine ; the acidic fermentation of sugars associated with the production of lactic, citric, or butyric acids ; the biochemical oxidation of alcohol to acetic acid (vinegar) ; the fermentation of carbohydrates emanating from starch so as to produce butyl alcohol and acetone ; the degradation of celluloses by specific types of micro-organisms ; and, finally, the hydrolytic action of lipase as utilised in the hydrolysis or splitting of fats in the manufacture of fatty acids (soap) and glycerine.

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CHAPTER I

THE ALCOHOLIC FERMENTATION OF SUGAR

The manufacture of beers, wines and spirits is of great interest not only from its antiquity, but also from the amount of scientific study which it has received during the past hundred years; the work of Pasteur [1] in France, of Hansen in Denmark, of Horace and Adrian Brown [2] in England, as well as that of other investigators, has done much to improve the production and enhance the quality of the numerous varieties of alcoholic beverages. Nevertheless, the main problems in these industries differ somewhat from those with which we are concerned in this book, in that the products in question are more or less dilute solutions of alcohol, whose merit depends upon their particular flavour and (to some extent) odour, this being the resultant of a particular blend of comparatively small proportions of various subsidiary materials. The maintenance of a characteristic product therefore depends largely on the type of organisms present, the variety of raw material employed, and various other factors, whereas it is desired here rather to refer to cases in which a specific organism (or rather the enzyme or enzymes present therein) leads to the formation of definite chemical compounds in reasonably large yields.

So far as alcoholic fermentation is concerned, therefore, we need only perhaps consider the manner in which a sugar is transformed into ethyl alcohol (so far as this is at present understood), together with a few points concerning the production of industrial (*i.e.*, highly concentrated) alcohol by fermentation.

Dealing with the latter first, it is of course common knowledge that in practically all cases yeast is employed

as the means of fermenting cane sugar. Yeasts are minute plants belonging to the genus *Saccharomycetes*, of which there are very many species and varieties ; many of these, especially the wild yeasts, are by no means so efficient in producing alcohol as certain cultivated forms, although they tend to multiply at a faster rate than the latter, and consequently require careful exclusion from the commercial yeast cultures. The ordinary brewer's yeast is one or other variety of *S. cerevisiæ*, whilst a few other species are also cultivated for the production of specific types of beverage, *e.g.*, *S. ellipsoideus*.

So far as supplies of industrial alcohol are concerned, this commodity is largely produced in conjunction with the yeast industry ; that is to say, the cultivation of baker's yeast designed for employment in bread-making, etc. The conditions favouring the rapid growth of yeast are not quite the same as those obtaining in the manufacture of definite kinds of alcoholic liquor, but on the other hand active growth is accompanied by a comparatively vigorous fermentation, the dilution of the sugar (molasses) solution and the temperature of fermentation being on the whole somewhat lower than in many cases where the yeast is being used solely as a fermenting agent. After the yeast has been separated by filtration from the mash in which it has been grown, the dilute alcoholic solution is submitted to fractional distillation.

One of the first forms of more or less scientific fractionation still for this purpose was that designed by Coffey ; this was a pot still dealing with successive batches of the alcohol solution. Subsequently continuous stills were introduced : the theory of the working of the plate fractionation column has since been given by Soret and others, so that at the present time it is possible to design a continuous fractionating column for alcohol which will operate with practically theoretical recovery of the alcohol and at a very high heat efficiency. Different types of continuous alcohol

stills are associated with the names of such firms as Blair, Campbell and McLean, or Barbet et Cie, the main principle of which is that the dilute alcohol liquor is introduced into the lower part of a large plate-fractionating column, at the base of which a regulated current of steam is admitted ; the alcoholic liquor is usually pre-heated, by means of heat interchangers, with some of the hot vapours from a higher point in the system. Eventually at the top of the column the vapours pass into a condenser (or two condensers in series), the condensate from which is partially returned to the top plate of the column as a reflux, whilst the remainder is drawn off in the form, usually, of about 92 per cent. alcohol. It is possible, by increasing the number of plates, to increase the concentration of the alcohol produced to 96 per cent. ; but, in view of the vapour-pressure curve for mixtures of alcohol and water, it is not possible by simple fractional distillation to obtain alcohol containing less than 4 per cent. of water.

Having thus briefly glanced at the main points which differentiate the production of industrial alcohol from the production of potable liquors, we will pass on to consider some modern views as to the mechanism of alcoholic fermentation, with particular reference to their bearing on means of modifying this process so as to yield products other than alcohol.

In his classical investigations on fermentation, Pasteur drew attention to the constant presence of small quantities of glycerine and succinic acid in the products of fermentation of grape sugar ; glycerine is normally found to the extent of about 3 per cent. of the total sugar fermented. Whilst the succinic acid is at present considered to be derived from the fermentation of small amounts of amino-acids, the glycerine appears to originate directly from the sugar. The precise stages by which sugar is degraded into alcohol and other products have still to be definitely proved, but a suggestive sequence of actions put forward by Neuberg [3] in 1913, whilst by no means fully accepted by

all workers in this field, would appear to be the most consistent explanation suggested up to the present.

Before discussing the Neuberg scheme, it should be made quite clear that the fermentation of carbohydrates to alcohol, etc., is a sequence of chemical actions in which enzymes of different specific characters and properties play essential parts. If, for a moment, we go back a step further than the sugar stage and consider the analogous fermentation of starch, we find that yeast is not capable of fermenting starch so readily as, for example, enzymes of malt. The hydrolysis of starch to disaccharides (maltose) is effected by a specific enzyme diastase (or, in modern nomenclature, malt amylase). Again, the further hydrolysis of the disaccharide to monosaccharides (glucose and fructose) results from the action of other enzymes. Thus maltose is only fermented by certain yeasts containing the enzyme maltase, which is able to convert this disaccharide into two molecules of glucose; whilst cane sugar is resolved into glucose and fructose by the action of the enzyme invertase, which is widely distributed in the vegetable kingdom in moulds, and also in many insects and animals and in most, but not in all, species of yeast. The conversion of the starch molecule into disaccharide and of the latter into monosaccharide, whilst involving complex molecules, is nevertheless chemically a simple change, consisting as it does simply in the addition of the elements of water; the necessity for employing different enzymes in different cases is simply a consequence of the fact that (as mentioned in Section I., Chapter III) enzyme and substrate have to be closely related in configuration before they are compatible.

Although we are dealing with a much simpler molecule when we come to the fermentation of a monosaccharide or hexose sugar, the stages involved in the chemical change which is usually summed up as

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

are far more drastic and complicated than simple actions of hydrolysis. Neuberg and his co-workers [3] suggest the following stages :—

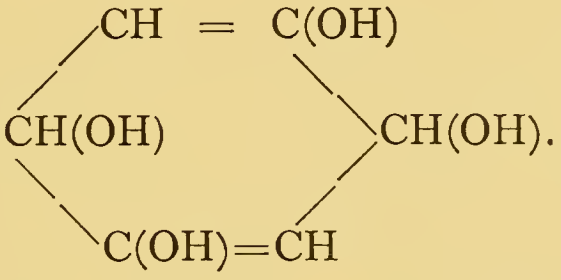
(i.) The withdrawal of two molecules of water from glucose giving the aldol of methylglyoxal

$$C_6H_{12}O_6 = CH_2 : C(OH).CH(OH).CH : C(OH).CHO + 2H_2O$$

followed by resolution of the latter into two molecules of methylglyoxal itself

$$CH_2 : C(OH).CH(OH).CH : C(OH).CHO = 2CH_2 : C(OH).CHO.$$

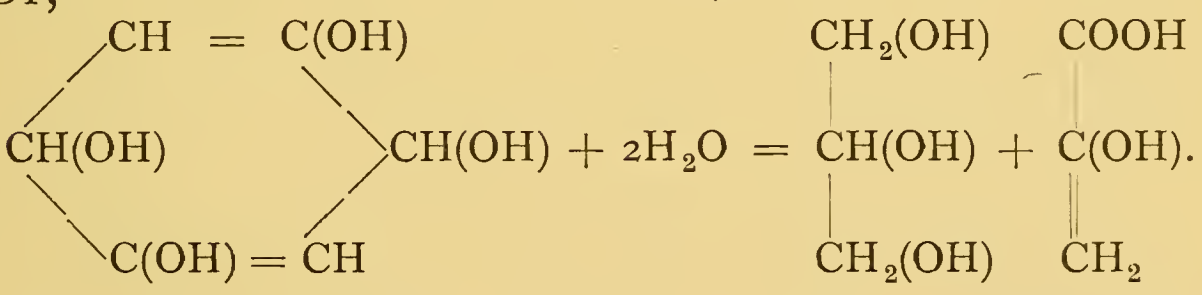
It may be noted that the methylglyoxal aldol could be written in the form of a symmetrical cyclic compound, namely



(ii.) The next stage is formulated as the conversion of two molecules of methylglyoxal (or of one of the aldol) into a molecule each of glycerol and of pyruvic acid :—

$$CH_2 : C(OH).CHO + H_2O + \begin{matrix} H_2 \\ | \\ O \end{matrix} = CH_2(OH).CH(OH).CH_2(OH)$$
$$CH_2 : C(OH).CHO \qquad\qquad CH_2 : C(OH).COOH$$

Or,



(iii.) The pyruvic acid is then broken down into acetaldehyde and carbon dioxide by means of a definite enzyme, termed by Neuberg and Kerb [3] carboxylase :—

$$CH_2 : C(OH).COOH = CO_2 + CH_2 : CH(OH)$$

(iv.) Finally from a fresh molecule of methylglyoxal and acetaldehyde, simultaneously oxidised

and reduced by the elements of water, there results a molecule of alcohol and, again, a molecule of pyruvic acid :—

$$\begin{matrix} CH_2:CH(OH) \\ CH_2:C(OH).CHO \end{matrix} + \begin{matrix} H_2 \\ | \\ O \end{matrix} = \begin{matrix} CH_3.CH_2(OH) \\ CH_2:C(OH).COOH. \end{matrix}$$

Some of the main points in support of this theory are the definite proof that acetaldehyde can be fixed during alcoholic fermentation, if an appropriate compound is present which will remove the aldehyde as fast as it is formed. For example, the presence of sulphites leads to the isolation of acetaldehyde, in high yield, in the form of the familiar acetaldehyde sodium-bisulphite compound, whilst other compounds, for example, dimethyldihydroresorcinol, are equally efficacious in fixing the aldehyde as a condensation product (Neuberg and Reinfurth).[3] It may be added that, in similar fermentations of sugars by moulds and bacteria (not necessarily leading mainly to alcohol, but tending to the production of acidic products), the intermediate formation of acetaldehyde has been detected, whilst pyruvic acid itself has likewise been fixed by means of a biochemical condensation with β-naphthylamine. In another form of fermentation which may be made to take place under feebly alkaline conditions, the aldehyde is said by Neuberg and Hirsch[3] to appear finally in the form of ethyl alcohol and acetic acid.

The three main variants of alcoholic fermentation outlined above may therefore be grouped as follows :—

(i.) Normal fermentation in faintly acid solution.

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

(ii.) Fermentation in presence of sulphite or other compound capable of fixing acetaldehyde by condensation.

$$C_6H_{12}O_6 = C_3H_5(OH)_3 + CH_3CHO + CO_2$$

(iii.) Fermentation under feebly alkaline conditions.

$$2C_6H_{12}O_6\ (+\ H_2O) = 2C_3H_5(OH)_3 + 2CO_2 + C_2H_5OH + CH_3COOH.$$

As will be shown below, in discussing the production of glycerine from sugar by fermentation, both the second and third of these types can be realised in technical practice.

Objections to these views have been raised mainly on the grounds that pyruvic acid *per se*, and also acetaldehyde, is not so readily fermented by yeast as glucose, and moreover, that pyruvic acid itself is certainly toxic to yeast; Neuberg counters this by pointing out that pyruvic acid is labile in character and able to exist in several tautomeric forms. It is, in fact, reasonable to believe that the various intermediate compounds concerned, at the moment of production by enzyme action, will not exist in the stable forms in which they are familiar as laboratory specimens. The case seems to be exactly parallel to the production of hexoses from carbon dioxide and water in the living plant or by artificial photosynthesis; in this case it is certain that "formaldehyde" is an intermediate stage in the process, and yet it is exceedingly difficult to obtain positive proof of the transitory existence of formaldehyde in the living cell.

Such compounds undoubtedly exist at the moment of their biochemical formation in forms which are not the same as the normal stable compounds which we associate with the respective terms; whether the difference is simply one of isomeric (tautomeric) form, or whether it is connected with a difference in the energy content of the molecule when produced *in vivo*, need not be further considered here. In order, however, to indicate more clearly that the stable forms of the intermediate products are not implied in the foregoing scheme, the latter have been expressed throughout in their enolic forms and,

alternatively, as derived from a possible cyclic form of the methylglyoxal aldol.

The Technical Production of Glycerine by Fermentation of Sugar.

The second and third types of Neuberg's theoretical scheme of sugar fermentation were first applied in technical practice during the war of 1914–1918, when the Central Powers were suffering from shortage of imported fatty materials. A process was worked out by Connstein and Lüdecke,[4] of the Vereinigte Chemische Werke, who found that it was possible to ferment yeast in presence of considerable proportions of sodium sulphite, and that a technical yield of 20–25 per cent. of glycerine on the sugar consumed could be obtained. The output of glycerine from beet sugar by this process in Germany and Austria reached as much as 800–1,000 tons per month at one period of the war. Towards the end of the war Eoff, Linder and Beyer[5] in America studied the similar fermentation in presence of dilute alkali solution (sodium carbonate or phosphate), and found that satisfactory yields of glycerine were also obtainable by this method. So far as the present application of the process is concerned, it is stated that a large plant for the production of glycerine from sugar is in operation in the United States, but elsewhere it does not seem that at the moment the method is being widely used. At the present time the supply of glycerine from fats, hydrolysed for use in the soap or other industries, appears ample for the demands of the market; but it may certainly be affirmed that in the event of any undue shortage of glycerine from fatty sources (with consequent rise in price), the sugar fermentation process is likely to prove an effective controlling factor.

In the German sulphite process, a 10 per cent. solution of glucose or cane sugar (molasses), containing neutral sodium sulphite equal in amount (as anhydrous

salt) to 40 per cent. of the sugar present, is fermented in the usual plant with ordinary brewer's yeast (*S. cerevisiæ*). The action is slower than under ordinary conditions, and requires about forty-eight to sixty hours at 30° for completion. The carbon dioxide formed at first interacts with the sodium sulphite to form an equilibrium mixture of sulphite, bisulphite, and bicarbonate :—

$$CO_2 + Na_2SO_3 + H_2O \rightleftharpoons NaHSO_3 + NaHCO_3$$

When equilibrium is attained (neutral sulphite still being present), the remainder of the carbon dioxide is evolved in the gaseous state.

The yeast can be filtered and used again, providing that intermediately it is employed in a normal fermentation under feebly acid conditions ; fresh yeast is then obtained by reproduction of the yeast cells, whereas during the sulphite or alkaline fermentations no yeast growth takes place.

The filtered mash is treated with lime and calcium chloride in order to remove the sulphite and carbonate present, and is preferably further clarified with a coagulant such as basic lead acetate, alumina ferric, or charcoal, in order to remove the somewhat abundant non-volatile and hydroxylated by-products.

The clarified liquor is first of all distilled in a fractionating column in order to recover the aldehyde and alcohol produced ; the residue from this distillation is then concentrated to crude glycerine, which is distilled for the production of dynamite glycerine by the customary methods. A thousand parts of sugar are stated to yield 230–250 parts of dynamite glycerine, 240–270 parts of alcohol, and 95–100 parts of acetaldehyde ; it is also claimed that starting from crude molasses, sufficient alcohol and aldehyde can be obtained to cover the working costs of the process, leaving the value of the glycerine as clear profit.

The alternative American method is carried out somewhat similarly to the sulphite process, but it is recommended that a special variety of yeast, *S. ellipsoideus*

var. *Steinberg*, should be employed, and the alkaline salt is added gradually. Thus, a 17 per cent. sugar solution may be fermented at about 30° with the yeast, sodium carbonate equal to 1·25 per cent. of the weight of sugar present being added, and further additions of the carbonate being made as the fermentation increases in rapidity, until the total amount added is equal to 5 per cent. of the original sugar ; small quantities of ammonium chloride, potassium phosphate, and magnesium sulphate are also added as nutrients for the yeast. The fermentation requires four or five days for completion, and the mash is then filtered, boiled with lime and also coagulating agents, and worked up as in the case of the sulphite liquor.

No acetaldehyde is produced by this process, but the discoverers state that a yield of 20–25 per cent. of glycerine is produced, about half of which is recoverable as dynamite glycerine. The yield of alcohol is about 30 per cent. of the sugar consumed. The amount of non-volatile organic matter present in the fermented product is somewhat larger than in the case of the sulphite method, namely, about 20–25 per cent. by carbonate fermentation as against about 15–18 per cent. by sulphite fermentation.

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CHAPTER II

THE PRODUCTION OF CERTAIN ACIDS FROM SUGARS BY FERMENTATION

THE chief characteristics of the action of yeast on sugars have been described above, and these may be contrasted with the action of the enzymes present in many species of fungi (moulds), and of bacteria. Both of the latter classes of organisms contain many members which convert the common sugars into alcohol, usually along with other products; but in other cases the fermentation proceeds on quite different lines and gives rise to products, of which some are dealt with in subsequent chapters, whilst others, now to be considered, include a number of acids, notably lactic, butyric, citric, fumaric and oxalic acids.

From the technical point of view, the manufacture of lactic and butyric acids is almost exclusively conducted by the fermentation processes; that of citric acid from lemon juice, etc., is apparently about to be supplemented by its production from sugar by controlled fermentation in presence of specific mould cultures, whilst it should be possible, were there any demand for fumaric acid, to produce this by means of a modified citric acid fermentation.

Lactic acid is somewhat important industrially. Various lactates are used to a considerable extent as mordants in dyeing cotton and wool, and also in calico printing, whilst the acid itself is required in large quantities in the leather industries in preparing the skins after liming and prior to the actual tanning; it is also used, of course, in a pure form in pharmacy to some extent. Recently, certain esters of lactic acid have come into demand as solvents in the modern lacquer industry, and also find some application as fixatives for perfumes.

Butyric acid has not up to the present been in such wide demand, although some of its esters have a restricted use in the blending of a few perfumes and flavouring materials. There is, however, some likelihood that outlets for this acid in other directions may develop in the near future, and an efficient process for its manufacture would probably be welcomed.

The chief use of citric acid is as a flavouring material and acidulant, whilst, like lactic acid, its esters are increasingly used as fixatives in the perfume and similar trades. The supplies of the acid from natural sources, such as lemon juice, are somewhat restricted, and the price is consequently rather high ; therefore it would appear that here also there is room for a scientific application of a fermentation process.

The production of lactic and butyric acid from sugars under specific conditions has been known and applied more or less empirically for very many years, but, according to A. C. Chapman [1] and others who are familiar with the technology of the processes concerned, the latter are capable of much improvement by taking advantage of the modern developments in microbiology.

Before giving a number of outlines of the working methods used in the case of these three acids, a sketch may be given of the general nature of the chemical changes which are supposed to take place. In the case of lactic acid fermentation, the ultimate change approximates very closely to the equation :—

$$C_6H_{12}O_6 = 2C_3H_6O_3.$$

The lactic acid fermentation is one which proceeds best in presence of air, and is thus of an oxidising type. The exact mechanism of the change is unknown, but it may be pointed out that Neuberg's methylglyoxal, $CH_2 : C(OH).CHO$, is structurally related to lactic acid in that addition of the elements of water to methylglyoxal furnishes the latter substance :—

$$CH_2 : C(OH).CHO + H_2O \longrightarrow CH_3CH(OH).COOH.$$

The butyric acid fermentation, on the other hand, is anaerobic, that is to say, it proceeds in the absence of air ; Buchner and Meisenheimer [2] suggested that its production was due to the intermediate formation of lactic acid, but it is at present supposed that the more likely mechanism is a condensation and rearrangement of acetaldehyde somewhat as follows :—

$$2CH_3CHO = CH_3.CH(OH).CH_2CHO$$

$$CH_3.CH(OH).CH_2CHO \longrightarrow CH_3CH_2CH_2COOH.$$

There is also some evidence [3] that the similar aldol of pyruvic acid (rather than acetaldehyde) may be an intermediate product in the process :—

$$2CH_3.CO.COOH = CH_3.C(OH)\,(COOH)CH_2.CO.COOH.$$

Finally, the case of citric acid is interesting because it involves the formation of a branched carbon chain from the original straight hexose chain, a reaction which finds a parallel in the laboratory in the formation of parasaccharic acid,

$$CH_2(OH).CH(OH).C(OH)(COOH).CH_2.CH_2(OH),$$

from certain sugars in the presence of alkali.

Lactic Acid Manufacture.—Conversion of sugars into lactic acid is effected by a number of bacteria, the chief of which are several varieties of *Bacillus aceti lacti*, *B. lactis aerogenes* and *B. Delbrücki*. Most of these organisms grow very readily in milk, the casein and other nitrogenous matter of which provides particularly suitable nutrient material for the organism. In the case of sour milk, the lactic acid has been formed originally from the disaccharide lactose. The bacilli are, however, capable of attacking various sugars, including glucose, fructose, cane sugar and maltose. In the older tanning processes, the bating or deliming process was carried out by drenching the hides in an aqueous suspension of bran ; this bran-drenching process owed its efficiency to the production of lactic acid, by fermentation of sugars from the starch present

in the bran, that is, to the manufacture of lactic acid *in situ* in the bating process.

In the actual manufacture of lactic acid from sugar, potato starch, maize, rice starch, etc., may form the raw material. This is subjected to diastatic fermentation in order to produce maltose or cane sugar, and the disaccharide solution (containing about 8–10 per cent. of sugar) is first sterilised by exposure to a temperature of 95°–100° for an hour. It is then transferred to the fermentation vats, where it is maintained between 45° and 55°. Fermentation is started by inoculation, either with a culture from a previous fermentation, or by a fresh culture prepared from soured milk. It is necessary to have ample supplies of nitrogenous matter present as nutrient for the bacteria, either in the form of natural protein matter (*e.g.*, bran or malt extract), or else by the use of appropriate inorganic salts, including ammonium salts, with a subsidiary amount of nitrates. Again, the organisms cannot tolerate more than about 0·5 per cent. of free lactic acid in the fermenting medium, and therefore the fermentation is conducted in presence of a suspension of chalk sufficient in amount to maintain the solution nearly neutral throughout. The fermentation should be complete in the course of from three to six days.

At the end of this time the fermented liquor (containing calcium lactate in solution) is settled and evaporated to about one-sixth of its bulk, after which it is decomposed with the theoretical amount of sulphuric acid, the precipitated calcium sulphate is removed by filtration, and the resulting solution concentrated *in vacuo* at about 60°. The commercial acid is usually sold at a strength of about 80 per cent. lactic acid.

Under good working conditions the yield of lactic acid from hexose sugar approaches the theoretical, that is to say, 100 parts of glucose will yield at least 90 parts of lactic acid : starting from starch, the yield is usually somewhat less—100 parts of maize or potato

starch furnish as a rule about 70–80 per cent. of lactic acid.

Butyric Acid Manufacture.—As already stated, the butyric acid fermentation of sugars is essentially an anaerobic process, and is characteristic of many of the putrefactive bacteria. Pasteur was the first to define an organism which conditions its production, and showed that the bacillus in question was present in decaying cheese, which, inoculated into a glucose solution, produced considerable proportions of butyric acid. It was subsequently found that many types of anaerobic bacteria, including those which are pathogenic to human beings and animals, induce the butyric fermentation; of those which are less markedly pathogenic the most active butyric acid producers are *Bacillus butyricus*, *B. amylobacter*, *Clostridium butyricum*, and various *Granulobacter* species.

In order to produce fermentation butyric acid on a technical scale, a solution containing up to 10 per cent. of glucose or cane sugar should be inoculated with a culture of one or other of the foregoing organisms, and fermented at about 30°–35° in vessels from which air is excluded as far as possible. Fermentation is usually complete in the course of 8–10 days, and the yield of butyric acid produced may be of the order of 30–40 per cent. In addition to butyric acid, various by-products are formed, including almost always more or less alcohol, carbon dioxide, and, as a rule, varying amounts of hydrogen, with subsidiary amounts of lactic acid, butyl alcohol, acetone, and other products. As in the case of lactic acid, the acidic products are toxic to the bacteria, and fermentation should therefore be conducted in the presence of chalk, in order to reduce the acidity of the solution to a minimum.

The butyric acid is recovered from the fermented liquor by a preliminary distillation of the latter in order to remove volatile non-acidic products, followed by decomposition of the calcium butyrate with the

correct amount of sulphuric acid, and subsequent steam-distillation and concentration of the butyric acid.

The butyric acid fermentation industry is, by comparison with the other processes described, in a more or less rudimentary stage, and as the demand for this product increases, the process will doubtless be overhauled and set on a more scientific basis.

Citric Acid Fermentation.—The production of citric acid has already been said to be conditioned by moulds ; the latter contain, as a rule, a wide variety of enzymes, with the result that the decompositions induced by them are very complex and lead to many products. By suitable cultivation, however, definite moulds have been produced which have the power of converting glucose very largely into citric acid, *e.g.*, in yields of 50–80 per cent. Whilst various species of *Aspergillus* yield citric acid amongst other products, the moulds which lead to the highest yields of citric acid are species of the genus *Citromyces*, *C. citricus* (Mazé and Perrier) [4] being one of the most efficient. If a sugar solution containing ammonium nitrate as nutrient for the organism is inoculated with a culture of this mould and maintained at an acidity of about p_H 3·5 at the ordinary temperature or somewhat higher, the formation of citric acid proceeds fairly smoothly, but slowly, to an extent approaching a 70 per cent. yield of the sugar present ; as in the previous cases the acidity of the solution is best controlled by the addition of calcium carbonate.[5]

If the action proceeds too far, or if certain other varieties of mould, for example, *Aspergillus fumaricus*, are employed, the main product of the reaction may be fumaric acid,[6] and there is no doubt that the biochemical manufacture of fumaric acid could be readily achieved were there any demand for this product. Also, either form of fermentation is liable to give rise to further more drastic decomposition with the final production of oxalic acid.

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CHAPTER III

THE PRODUCTION OF VINEGAR BY BIOCHEMICAL OXIDATION OF ALCOHOL

THE manufacture of vinegar is, of course, practically as old as that of potable alcoholic liquors, but the scientific explanation of its formation from the latter was commenced by Pasteur from about 1860 onwards. He showed that the change was brought about by an organism to which he gave the name *Mycoderma aceti*. Later investigations by Hansen, and notably by Adrian J. Brown (1886–7), have proved that a large number of bacteria are capable of oxidising alcohol to acetic acid, and that different forms occur, one or other often predominating in specific localities or breweries, some being perhaps more rapid in action or more resistant to external conditions than others. All, however, exercise practically the same chemical function, namely, the oxidation of alcohol to acetic acid (and, eventually, of the latter to a certain extent to carbon dioxide and water); but different organisms appear to some extent to tend to the formation of somewhat different by-products, which, although produced in very small proportions, confer a distinctive flavour and odour on the resulting products. The most definite of these organisms are Hansen's *Bacterium aceti*, which is commonly present in the German breweries, and Brown's *B. xylinus*, which is the main organism usually present in vinegar factories in this country.

The acetifying organisms are bacteria which, under favourable conditions, grow very rapidly and form thick, tough, gelatinous films consisting largely of a cellulose-like nitrogenous material in which the bacilli are enclosed. The organisms are relatively resistant

to both alcohol and acetic acid, and will tolerate up to 10 per cent. of alcohol, although acetifying action proceeds most readily when the alcohol concentration is below about 5 per cent. Their maximum activity is attained when the acetic acid concentration is between 2 and 3 per cent., although production of acetic acid does not cease until the concentration of the latter has reached somewhat over 6 per cent.

Bertrand found that the acetifying bacteria also have the property of converting certain polyhydric alcohols related to the sugars into the corresponding α-ketoses, $R.CO.CH_2OH$, and referred to this type of ferment as the sorbose bacterium; thus these organisms convert glycerol into dihydroxyacetone, mannitol into fructose, sorbitol into sorbose, but are without action on certain other alcohols, such as glycol or dulcitol.

Like many other old-established industries in which efficiency had perforce to be attained by empirical methods, the vinegar industry has perhaps been somewhat slow to apply the results of the work of the bacteriologist. The procedure employed varies a good deal from one country to another, and even the raw material is not the same. Since, so far as regards catalytic action, the industry has no specific points of interest other than, for example, those which have already appeared in connection with the other acid fermentations and the ordinary alcoholic fermentation dealt with in the preceding chapters, it is only necessary here to indicate very briefly the chief features of the more important vinegar processes.

The raw materials employed as a source of vinegar may be either sugars (starch) or alcohol itself, and thus the industry may be divided into two classes, namely the manufacture of malt vinegar and of wine vinegar.

Malt Vinegar.—Malt vinegar is the modern form of the industry, and has probably only been practised for a mere 300 years. Essentially this refers to the production of vinegar from beers and ales as distinct

from wines ; and in the first place, vinegar was probably made as a waste-product from ales which had turned sour, which were therefore acetified completely by addition of the "vinegar plant" (*i.e.*, the tough gelatinous film referred to earlier). Later it became the custom, which has persisted in most vinegar works, to commence the production of vinegar from malt or, in some cases, rice or maize. The preliminary fermentation of the starchy material is carried out in much the same way as in the production of beer, a diastatic fermentation being first carried out in a mash tun, whilst in some cases hydrolysis of the starch with dilute mineral acid is resorted to, followed by neutralisation with chalk.

The wort thus obtained is cooled and inoculated with yeast and fermented at a higher temperature than in the case of beer manufacture (22°–24°) for about three days. The object of the higher temperature is to produce more complete conversion to alcohol ("attenuation," *i.e.*, lowering of the specific gravity of the wort due to conversion of sugar into alcohol). The fermented wort, known in the trade as gyle, is frequently stored for a considerable period, when it commences to become acid and thus saves time in the actual acetification.

It should also be noted that the acetifying bacteria are themselves associated with an amyloclastic enzyme, so that they can directly effect the conversion of malt starch into acetic acid. In practice, however, this is usually carried out separately as has been described. The actual biochemical oxidation of alcohol to acetic acid is carried out in vessels which are known as acetifiers, and, so far as this part of the process is concerned, the method is similar in the case of both malt and of wine vinegar ; we may therefore deal with both processes at the same time.

Wine Vinegar.—This is the oldest type of vinegar, and was made originally by filling oaken casks with sour wine to which a little vinegar from a previous

fermentation was added. The casks were left on their sides in warm well-ventilated sheds kept at about 25°. The fermentation required a prolonged period for completion, and under good conditions a cask of about 100 gallons capacity would produce about twice this volume of vinegar per year.

A more rapid method for production of wine vinegar consists in operating the process in fermentation units, consisting of two large upright open casks about 9 ft. high by 4 ft. in diameter, fitted with a perforated false bottom or tray about a foot from the base. On this perforated plate is placed a heap of beech shavings, vine-stalks or similar material, designed to expose a large surface for the support of the fungus, and also to provide a favourable medium on which it can develop fully. In carrying out a fermentation, one of the vats is completely filled and the other only half filled with sour wine; oxidation proceeds more vigorously in the half empty cask, and at daily intervals the latter is filled up from the full cask, which is thus left half empty, and in which consequently the fermentation is then accelerated.

In the most modern practice, however, larger acetifiers are employed which are of similar design to those used in the malt vinegar industry.

Modern Acetifiers.—The acetifiers now employed have a capacity of from 3,000 gallons upwards, and consist of rectangular tanks fitted with perforated false bottoms, and packed either with shavings or basketwork as in the older system, or with a series of wooden frames so arranged that the free space between each wooden slat is only about $\frac{1}{4}$ in. In these acetifiers the fermented wort or gyle is circulated in a fine shower from the top of the vat downwards and meets, on its downward passage over the framework or basketwork (which as usual serves as the main support for the bacteria), a current of air which is passed upwards from the base of the vessel through air holes situated below the perforated false bottom. It is essential

that the total area of the air holes should be approximately the same as the area of the vents through which the spent air leaves the top of the vat. This is in order to ensure that the air on its passage upwards through the acetifier should be evenly distributed and should not give rise to channelling; it is obviously of the greatest importance to ensure that an adequate supply of oxygen is available in order to obtain the most efficient oxidation. The contents of the acetifier are maintained at a much higher temperature than in the old methods: fermentation is usually carried out at about 40° (or slightly above) in English factories (malt vinegar), and at 30°–35° for wine and spirit vinegars on the Continent. The process should be complete in twenty-four hours, and the vinegar is then ready for storage, during which a certain amount of settling and clarification occurs; after about three months' storage in vats the crude vinegar is filtered and is then ready for use.

It should be mentioned that acetification is frequently conducted in stages, as it is found that by acclimatisation the acetifying bacteria can be made more resistant to higher concentrations of acetic acid. The process is therefore usually carried out in stages in separate acetifiers in which the concentration of acetic acid is successively brought up to about 6, about 9–10, and finally to as much as 12 per cent. of acetic acid.

Malt vinegar is of a characteristic brown colour, and possesses an odour due to the presence of small amounts of specific esters; its content of acetic acid in England is usually somewhat over 4 per cent., and in Germany about 6 per cent. Wine vinegar, on the other hand, has a more definitely alcoholic odour, is pale yellow to reddish in colour, and usually contains 8–12 per cent. of acetic acid.

Other trade qualities of vinegar, such as wood vinegar, or distilled white vinegar, may of course in many cases not be from a fermented source at all, but simply

dilute solutions of acetic acid coloured with caramel, to which sometimes small quantities of flavouring materials may have been added.

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CHAPTER IV

OTHER FERMENTATION INDUSTRIES BASED ON STARCH OR CELLULOSE

In the previous chapters we have seen that sugars (or starch) can be converted into ethyl alcohol by means of yeasts, and that by suitable modification of the external conditions alcoholic fermentation can be diverted so as to produce large yields of glycerine and acetaldehyde; further, certain specific bacteria and moulds are able to transform sugars into one or other of a number of common organic acids, notably lactic, butyric and citric acids. There remain to be discussed one other very important type of sugar fermentation based on starch, and a number of instances in which cellulose material undergoes fermentation, either as such or after preliminary conversion by acids into soluble sugars.

The Butyl Alcohol-Acetone Fermentation of Starch.

The presence of small quantities of acetone and butyl alcohol in the products of fermentation of carbohydrates by bacterial action had been recognised for many years when Fernbach succeeded, in 1910, in producing cultures of specific bacteria which possessed the power of almost completely transforming glucose into butyl alcohol, acetone, hydrogen and carbon dioxide. Organisms of the Fernbach type are able to effect fermentation of potato starch, and the Fernbach process was in operation as early as 1912 with a view to produce butyl alcohol from potato starch in order to obtain raw material for the manufacture of butadiene for a proposed commercial synthesis of rubber. In 1916, when acetone was in tremendous demand for cordite manufacture, work on this process was intensively revived from the point of view of pro-

duction of the latter product. In the hands of Weizmann a new bacillus was isolated, which was able to effect the fermentation of starch from maize, rice and other forms of seed, such as, for example, horse-chestnuts and acorns. This process was operated, especially in Canada and the United States, on such a scale that during the later war years it became the main source of production of acetone.

The relative amounts of the organic products formed, however, are two parts of butyl alcohol to one of acetone, and in consequence huge quantities of fermentation butyl alcohol were accumulated, for which at the time there was little outlet. At the present time, ten years later, the position is exactly reversed : the nitrocellulose lacquer industry has developed on a very large scale, and butyl alcohol is one of the most suitable media in which to apply these lacquers. Consequently this fermentation process is at present worked primarily with a view to producing *n*-butyl alcohol whilst acetone is of the nature of a by-product and is available in sufficient quantity to satisfy most of the present market demand. The later development of the fermentation process has been most vigorously carried on in the United States and Canada, but factories are also in operation in England and on the Continent.

The relative merits of the Fernbach and Weizmann bacilli gave rise to considerable and somewhat heated discussions a few years ago, but it is probably a fair apportionment of credit to suggest that the original elaboration of the biochemical method leading to butyl alcohol and acetone is essentially the work of Fernbach and his collaborators at the Institut Pasteur, whilst it would appear that Weizmann succeeded in cultivating a form of organism which was somewhat more resistant than the earlier types to the fermentation conditions, and was thus able to deal with a wider variety of raw materials. Probably in present-day practice a bacillus of the type first cultivated by Weizmann is almost always employed.

The butyl alcohol fermentation is to be regarded as a specific process like the well-known alcoholic and lactic acid or butyric acid fermentations. The various types of bacteria which give rise to butyl or butyric fermentations are now grouped under the general name of *Clostridium butylicum*. The original forms employed were frequently species of *Granulobacter*, whilst the Weizmann bacillus was first termed *Bacillus butylicus*, but is now usually referred to as *Clostridium acetobutylicum*. The mechanism of the action has been discussed by a number of workers, including Thaysen [1] and co-workers, and Speakman.[2] It would appear to depend essentially on the primary production of butyric acid and acetic acid from glucose, somewhat according to the equation :—

$$C_6H_{12}O_6 = C_3H_7CO_2H + CH_3CO_2H + O_2.$$

The oxygen does not appear as such, and it is probably used up in converting butyric acid or similar substances by β-oxidation into acetoacetic acid and hydrogen. At all events, it seems certain that the immediate sources of butyl alcohol and acetone are respectively butyric and acetic (or acetoacetic) acids ; this view is reinforced by the observation that if butyric or acetic acid is added at suitable dilution to a mash undergoing active fermentation, the respective yields of butyl alcohol or acetone can be proportionately increased, whilst the active ferment is also capable of transforming other simple organic acids into the corresponding ketones or alcohols to some extent. A very rough approximation to the total products yielded by the normal butyl fermentation may be given by the equation :—

$$3C_6H_{12}O_6 = 2C_4H_9OH + (CH_3)_2CO + 7CO_2 + 4H_2 + H_2O.$$

The general development and mode of operation of the process may be gathered by referring to articles by Speakman [2] in 1919, and by Killeffer [3] and by Woodruff [4] in 1927. The first-named author gives a description of the Toronto plant which commenced

operation early in 1916. This plant consisted of fourteen fermenters, 18 ft. in diameter by 20 ft. high, each holding 24,000 gallons of fermenting mash. The raw material employed was mainly maize corn, and this was prepared for fermentation by agitation with water in mash tuns at about 50°. After shaking the necessary amount of maize meal slowly and evenly into the charge of water and heating subsequently for about 30 minutes, during which the temperature was brought to the boiling point, the mash was passed into cookers (steel tanks holding 8,000 gallons), in which it was maintained at about 10 lb. pressure of steam for over an hour in order to effect complete sterilisation. From the cookers the sterilised mash passed through a specially-designed cooler, arranged to deliver cooled mash to the fermenters at 37·5°. The fermenters were then charged from the cookers until there were 24,000 gallons in each, and then inoculated with the culture which had been prepared under laboratory conditions in an active state, and the fermentation commenced.

Bacteria are in general much more sensitive to deterioration, especially by infection with alien organisms, than the yeasts, and probably the most important point in the whole process is to destroy the microflora present in the original mash, and, after the latter has been sterilised, to cool it and ferment it under strictly sterile and aseptic conditions. In the early stages of this process, especially in the rush of war conditions, when attempts were made to transform ordinary alcohol distilleries into butyl alcohol-acetone fermentation plants, many difficulties were encountered, the majority of which were undoubtedly caused by infection.

That the problems had been satisfactorily dealt with even during the war period is evident from Speakman's statement that of 3,458 fermenters inoculated (each holding 24,000 gallons of mash), between April, 1916, and November, 1918, none was rejected and not distilled.

The output of products from a plant of this type may

be estimated when it is remembered that maize with a content of about 60 per cent. of starch yields 14 per cent. of butyl alcohol and 7 per cent. of acetone in commercial practice. The 1927 papers indicate that the present production of butyl alcohol and acetone in America amounts to about 60 tons of butyl alcohol, 30 tons of acetone and 1 ton of accompanying alcohol per day. This involves the daily consumption of 25,000 bushels of maize corn and a corresponding production of about 6,000,000 cub. ft. per day of by-product gas, of which 2,500,000 cub. ft. is hydrogen and the remainder carbon dioxide.

The modern fermenters hold 40,000 gallons of 8 per cent. maize mash, the number of fermentations thus commenced per day being between forty and fifty. Each fermenter is inoculated with pure cultures of *Clostridium acetobutylicum*, the acidity of the mash (as in the earlier methods of operation) is maintained at p_H 4·3, and fermentation is complete in from 2–3 days at about 37·5°. The maximum evolution of gas is obtained about half-way through the fermentation, and is of the order of 8,000–10,000 cubic feet per hour. This gas in the most modern plants is passed through beds of adsorbent charcoal in order to recover small proportions of volatile organic products present therein ; the daily yield from 4,000,000 cubic feet of gas amounts to over a ton of a mixture containing 55 per cent. acetone and 22·5 per cent. each of butyl and ethyl alcohols.

Suggestions are now being made to utilise the stripped gas industrially, since it consists of hydrogen in a remarkably pure condition and is suitable for catalytic purposes. It is proposed to remove the carbon dioxide by solution in water under high pressure in the ordinary way, and to use the gas for ammonia or methyl alcohol synthesis ; incidentally it is stated that carbon dioxide can be used for the latter in place of carbon monoxide, according to the equation :

$$CO_2 + 3H_2 = CH_3OH + H_2O.$$

The preparation of the *Clostridium acetobutylicum* culture is carried out with the utmost care from spores, in five successive stages, before it is put into the fermenters; cultures not more than six days old have been found best for use in plant practice. The activity of each batch of culture is carefully tested, both throughout its preparation and before use in a 40,000-gallon fermenter. The bacillus, it should have been mentioned, contains its own amylase, which effects the conversion of the maize starch into glucose, the latter then being converted, as described, into the various products.

The ferment mash (which originally contained 8 per cent. of maize starch), finally contains 2·5 per cent. of the organic solvent products and passes from the fermenters to a reservoir, from which it is pumped to continuous beer stills. These are columns 54 ft. high by 8 ft. diameter, which furnish the mixed solvent in the form of a 50 per cent. aqueous solution. This solution separates into two layers, one containing mainly butyl alcohol with some acetone, alcohol and water, whilst the other is an aqueous layer containing relatively large amounts of acetone and alcohol and relatively little butyl alcohol. Each layer is treated separately in discontinuous fractionating columns, which deliver the respective products in a state of sufficient purity for technical use.

This modern fermentation process is the one which conveys the impression most forcibly that there is obvious scope for the development of similar processes, some of which might well lead to equally successful and important outputs of useful products.

Some Aspects of the Fermentation of Cellulose.

Up to the present, cellulose has not been made the starting point for the production of specific chemical compounds by direct fermentation, but the fermentation of cellulose either as such or after conversion into fermentable sugars by means of mineral acids

is an important problem which concerns a number of widely differing industries.

In the first place, the conversion of cellulose into fermentable sugars has a direct bearing on the potential production of industrial alcohol, and is receiving consideration more especially from the point of view of the manufacture of alcohol as a source of motor power in districts where waste cellulose (dried grass, straw, sawdust, etc.) is abundant, and in which natural supplies of oil or coal are deficient. This problem, however, is not being attacked so much by attempts at direct fermentation of cellulose as by preliminary hydrolysis of the cellulosic materials by means of aqueous mineral acids ; this treatment of cellulose will receive attention in Section IV., Chapter II, pp. 311–313, whilst the conversion of the sugars thus produced into alcohol is simply a case of the ordinary alcoholic fermentation referred to in Chapter I of this section (pp. 247–254).

On the other hand, a certain amount of work has been carried out, not only in the laboratory, but on the semi-technical scale on the lines of direct fermentation of cellulose, and a bacillus has been found which is capable of rapidly attacking almost every form of cellulose under either anaerobic or aerobic conditions. The most convenient source of the bacillus in question (which does not appear to be definitely classified) is steaming stable manure. It grows most rapidly at 60°–68°, but attacks cellulose steadily at any temperature between about 35° and 70°. The extraordinarily high temperature at which this bacillus reaches its maximum activity has led to its being referred to as a thermophilic organism, and for practical use, a temperature of 68° automatically maintains the culture in a pure condition, as the usual types of ferment are completely destroyed at this temperature.

It may be pointed out that the study of direct fermentation of resistant cellulose goes back to 1875

(Popoff) and 1883 (Hoppe-Seyler); these workers found that filter paper cellulose could be fermented with formation of methane. Omelianski [5] (1895–1902) and Pringsheim [6] (1902) extended this work and indicated that alcohol and acetic acid were also produced during cellulose fermentation. Omelianski's work was carried out at the usual temperature of about 35°, whilst Macfadyen and Blaxall [7] first drew attention to the action of thermophilic organisms on cellulose at about 60°, and Pringsheim [6] amplified this observation, noting that hydrogen, carbon dioxide, formic and acetic acids were produced at 55°–60°. In the past few years the subject has received increased attention, mainly from the point of view of power alcohol, and from the work of Langwell,[8] Thaysen [9] and others, it is to be inferred that high temperature fermentation is due to practically one form of bacillus, but that the products vary with the conditions of fermentation, including the temperature, the aerobic or anaerobic conditions employed, etc. Langwell, working with cellulose from sulphite pulp, filter paper, cotton waste or rice-straw gives the following range of possible products :—

	Per cent.
Acetic acid . . .	20–80
Butyric acid . .	0–30
Lactic acid . . .	0–60
Alcohol	0–30
Hydrogen . . .	0– 1
Carbon dioxide . .	28–50
Methane	0– 8

Free aeration appears to favour the production of ethyl alcohol, whilst with limited aeration acetic acid tends to be the main product.

The formation of the various products is capable of explanation, according to Langwell, on lines sug-

gested by Neuberg's hypothesis in the case of yeast fermentation, somewhat as follows :—

(1) $C_6H_{10}O_5 + H_2O = 2CH_3CO.COOH + 2H_2$.
(2) $CH_3CO.COOH + H_2 = CH_3CH(OH).COOH$.
(3) $CH_3CO.COOH = CH_3CHO + CO_2$.
(4) $CH_3CHO + H_2 = CH_3CH_2OH$.
(5) $2CH_3CHO + H_2O = CH_3CH_2OH + CH_3COOH$.
(6) $2CH_3CH_2OH = CH_3COOH + 2CH_4$.
(7) $C_6H_{10}O_5 + H_2O = 3CH_3COOH$.
(8) $2CH_3CH(OH).COOH = CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$.

Thus although the problem of conversion of the complex and varied cellulose derivatives into simple products by direct fermentation is very difficult, there is reason to believe that sufficient control of the process is being reached to afford definite commercial possibilities. It should be mentioned that a not inconsiderable proportion of the celluloses (hemi-celluloses) are derived from pentose sugars, and that the latter, although not fermented by yeast, etc., are decomposed by various specific types of bacteria with production of ethyl alcohol, acetic acid, etc.

Apart from ultimate breakdown to simple derivatives such as alcohol, methane or acetic acid, fermentation processes play a considerable part in other industries connected with cellulose. Thus the process known as retting, usually in reference to flax and also employed with other cellulose fibres, consists in the decomposition of the pectins or gum-like components of the plant tissue which surround or are surrounded by the fibrous cellulose tissues. The pectin substances are much more readily attacked by the bacteria present in decaying vegetable matter than the cellulose fibres, and in preparing flax or other material for use in the textile industries it is subjected to a fermentation process, as a result of which the pectins are converted into soluble substances, leaving the cellulose fibres in a condition suitable for spinning, etc.

Finally, reference should be made to an important process, introduced into agriculture as the result of the bacteriological researches of Hutchinson[10] and his colleagues at Rothamsted. These investigators have found that the decomposition of waste vegetable matter giving rise to the black sticky substance known as humus (which is of extreme importance in soil fertility) is effected most efficiently by a specific micro-organism, *Spirochœta cytophaga*, of which they have isolated pure cultures. This organism acts at about 30° under aerobic conditions; it is, however, very sensitive to the presence of organic nitrogen or of reducing sugars such as maltose or dextrose, but in presence of an adequate supply of air and of a supply of nitrogen (preferably in inorganic form) as food for the organism, together with an abundance of moisture, fermentation proceeds rapidly and in the course of a few months a heap of waste vegetable refuse is converted into a material resembling, in appearance and in nutritive value for the soil, well-rotted farmyard manure. Under the name of "Adco," a material containing the organism in question, together with appropriate supplies of nitrogenous food and similar materials, has been put on the market and is being used in increasing quantities by farmers and market gardeners for the purpose of converting waste vegetable material (straw, grass, leaves, etc.) into an adequate substitute for farmyard manure. The Adco process is of especial interest in its direct application of biochemical catalysis to one of the fundamental needs of agriculture.

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CHAPTER V

THE HYDROLYSIS OF FATS BY MEANS OF LIPASE

THE most widely employed method of resolving natural fats into their component fatty acids and glycerine is that of the ordinary soap-pan ; the greater part of the fatty acids used in industry is required in the form of soaps and in general the ordinary soap-boiling process, consisting of direct saponification of the fat with dilute alkali by boiling in open pans, is the most satisfactory. The low concentration of glycerine in the aqueous liquor or lyes from the soap-pans is, however, a minor drawback to the efficiency of the soap-boiling process, and certainly when the fatty acids are required, as such, for purposes other than soap (for example, in the manufacture of candles), it becomes somewhat cumbersome to proceed by means of saponification with alkali in a dilute aqueous solution. Consequently several alternative processes have been employed, by means of which the glycerine liquors, instead of containing only from 3–5 per cent. of glycerol, are obtained in the form of a 15–17 per cent. glycerine solution. One method is to carry out the fat hydrolysis in autoclaves, when the fats are hydrolysed by the action of steam at about 120°–140° in presence of a certain proportion of lime or magnesia (*cf.* Section IV., Chapter II, p. 314), whilst again, a suspension of fat in water at about 90°–100° may be hydrolysed fairly readily and smoothly by the use of a special hydrolytic agent known as the Twitchell[1] fat-splitting agent (*cf.* Section IV., Chapter II, p. 316).

The fatty acids produced by either of these methods are said to suffer from a tendency to assume a dark colour, but how far this is due to imperfectly under-

stood control of the processes is not quite certain; at all events the fatty acids obtained by the lipase process about to be described are usually of very good colour, whilst the concentration of glycerine in the aqueous liquors from the process reaches as much as 16–17 per cent.

It may be mentioned in passing that the Twitchell agent, referred to above, consists of a sulphonated mixture of a fatty acid and an aromatic hydrocarbon, which has the property of emulsifying mixtures of fat and water very readily. In other words, it is almost equally attracted, so to speak, by a fatty oil and by water, and in view of what is known at the present time with reference to the orientation of fatty acids, etc., at water surfaces, it is evident that the compound in question, when distributed in a fat-water system, will arrange or orientate its molecules so that the aliphatic part of the chain is attracted towards the fat, and the acidic radicles, especially the sulphonic group, towards the water. When the fat and water are mixed in presence of the Twitchell agent, therefore, molecules of water and of fat will definitely form part of the same system (fat : Twitchell–agent : water), and in presence of the strongly acidic sulphonic group hydrolysis is effected. The Twitchell agent is thus a somewhat close artificial or synthetic reproduction of a typical hydrolytic enzyme, and the similarity to a true enzyme is reinforced by the fact that its action is, to some extent, reversible.

Coming to the lipase process [2] itself, it may be observed that the enzyme lipase (or, at all events, lipoclastic enzymes) is widely distributed in nature, and is found in the seeds and other parts of vegetable tissue, and also in the pancreas, liver, brain, intestines, and other organs of animals. The source of the lipase used in technical fat-splitting is almost invariably castor-oil seeds, in which it is particularly abundant.

The castor-oil seeds are decorticated, carefully separated from fragments of husk and extraneous

matter, and then passed through a series of rollers, in which they are ground to a fine meal, which is intimately mixed on a perforated shaking screen with sufficient water to form a thick paste. This is centrifuged to separate the seed particles from the "seed milk" or aqueous emulsion; the latter is set aside at about 23°, and in a day or two fermentation sets in and the pasty emulsion separates into an aqueous layer and an upper layer resembling thick cream. The latter consists of an aqueous emulsion of castor-oil fatty acids holding the lipase in suspension, and is used as the hydrolytic agent.

The activity of the agent varies somewhat widely in different preparations; it has been suggested that the addition of a small proportion of sulphates of calcium or manganese to the ferment both activates and stabilises the preparation.

The fat to be hydrolysed should first be thoroughly clarified by boiling with dilute sulphuric acid, followed by settling and washing. It is then placed, together with about half its weight of water and about 7–10 per cent. of ferment cream (according to the degree of activity of the latter), in a wooden vat fitted with a perforated copper coil at the base, through which air or steam can be admitted. The charge in the vat is agitated with air through the coil until a stable emulsion results, and it is then left to stand for a day or more, during which time hydrolysis proceeds practically to completion (97–98 per cent.).

The process is best carried out in a room maintained at a temperature between 20° and 30°, this being the best range for lipase activity. The method is therefore most suited to soft oils, although tallows and hardened fats can also be handled if they are mixed with liquid fats so as to produce a semi-solid consistency at 20°–30°.

When hydrolysis is complete, the charge is agitated by means of steam in order to break up the emulsion as far as possible; sometimes it is necessary to use a

small amount of sulphuric acid at this point to aid in breaking the emulsion. On subsequent standing three layers are produced, the fatty acids on the top, an intermediate layer of emulsion (which manipulative technique must make as small as possible), and an aqueous layer containing the glycerine, and also a certain amount of colloidal organic matter emanating from the ferment. The clear layers are drawn off separately, and the residual emulsion is steamed with dilute sulphuric acid in order to recover more fatty acids ; whilst the clear fatty acids are washed once or twice by agitation with steam. As already stated, the colour of the fatty acids produced by this method is usually excellent.

The recovery of crude glycerine by concentration of the aqueous part of the product requires a certain amount of care, and it must be admitted that at present " fermentation crude," as it is termed, has not so good a reputation as crude glycerine produced from the autoclave or Twitchell processes of fat splitting. The lipase process has, however, not yet been employed very systematically or extensively, and it is probable that the quality of the glycerine liquor will be improved as the technique of the method is strengthened. Obviously the aqueous liquor from fermentation is always liable to contain more colloidal organic matter than in the other cases mentioned and, after preliminary neutralisation and coagulation with iron oxide or alumina in the ordinary way, it is well to pass the filtered clarified liquor through a bed of adsorbent charcoal or similar material prior to concentration. With an original fat of fair quality, a " fermentation crude " should then be obtained which, although usually dark-coloured, will not contain excessive amounts of ash and organic matter, and should be capable of distillation without serious difficulty.

The lipase process has been worked to a moderate extent in the United States and on the Continent, and its use should extend when methods of producing the

enzyme in a more stable state and less sensitive to variations in working conditions have been worked out, together with additional modifications for avoiding loss of fatty acids in the form of residual emulsion, and for reducing to a minimum the colloidal impurities which tend to pass into the aqueous glycerine layer.

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SECTION IV

HOMOGENEOUS CATALYSIS IN LIQUID SYSTEMS

THE industrial processes which fall under this heading can be divided primarily into two classes :—

1. Those in which the chemical action involved is essentially the addition to, or withdrawal from, a compound or compounds of the elements of water.

2. A wide variety of synthetic organic reactions employed in the dyestuffs and fine chemical industries, including " condensations " in which, as a rule, hydrogen chloride or bromide (or sometimes water) is eliminated from two organic molecules, the introduction of halogen substituents into organic compounds, and a few cases of catalytic oxidation. These processes are exceedingly numerous, and are only illustrated in the present work by a few important examples which are typical of the rest.

The processes embraced in the first class, however, subdivide themselves into three fairly well-defined groups :—

(*a*) *Actions of hydration*, *i.e.*, addition of the elements of water to one molecule, resulting in the formation of another molecular species. The fundamental technical processes with which we are concerned are :

(i.) The hydration of acetylene to acetaldehyde, and the subsequent conversion of this product (catalytically or otherwise), into a large number of synthetic aliphatic compounds of technical importance ; and

(ii.) The hydration of ethylene to ethyl alcohol.

(*b*) *Actions of hydrolysis*, *i.e.*, addition of the elements of water to a compound with resulting formation of two independent compounds, frequently an alcohol and an acid. This important section includes the conversion of starch and cellulose into simple sugars by the

action of mineral acids, the hydrolysis of fats by the "autoclave," Twitchell, and sulphuric acid hydrolysis methods, and the production of benzaldehyde and benzoic acid from benzal chloride and benzotrichloride.

(*c*) *Actions of dehydration*, including the removal of water from an alcohol and an acid to form an ester, the withdrawal of water from an alcohol and an aldehyde producing an acetal, and the loss of water by an alcohol leading either to an ether or an olefinic hydrocarbon.

Each of the classes mentioned forms the subject of a chapter within the present section.

Pedantically speaking, perhaps few of these catalyses are entirely homogeneous ; thus acetylene gas is passed into the liquid acid system, a gas or vapour product may result when an alcohol is dehydrated, and fats and water co-exist only as an emulsion. Yet it is tolerably certain that the actual catalytic changes discussed occur in a homogeneous liquid system, and for this reason they are appropriately treated in one and the same section.

CHAPTER I

THE INDUSTRIAL SYNTHESIS OF ALIPHATIC ORGANIC COMPOUNDS FROM ACETYLENE OR ETHYLENE

The Production of Acetaldehyde from Acetylene, and its Transformation into other Technically Useful Organic Compounds.

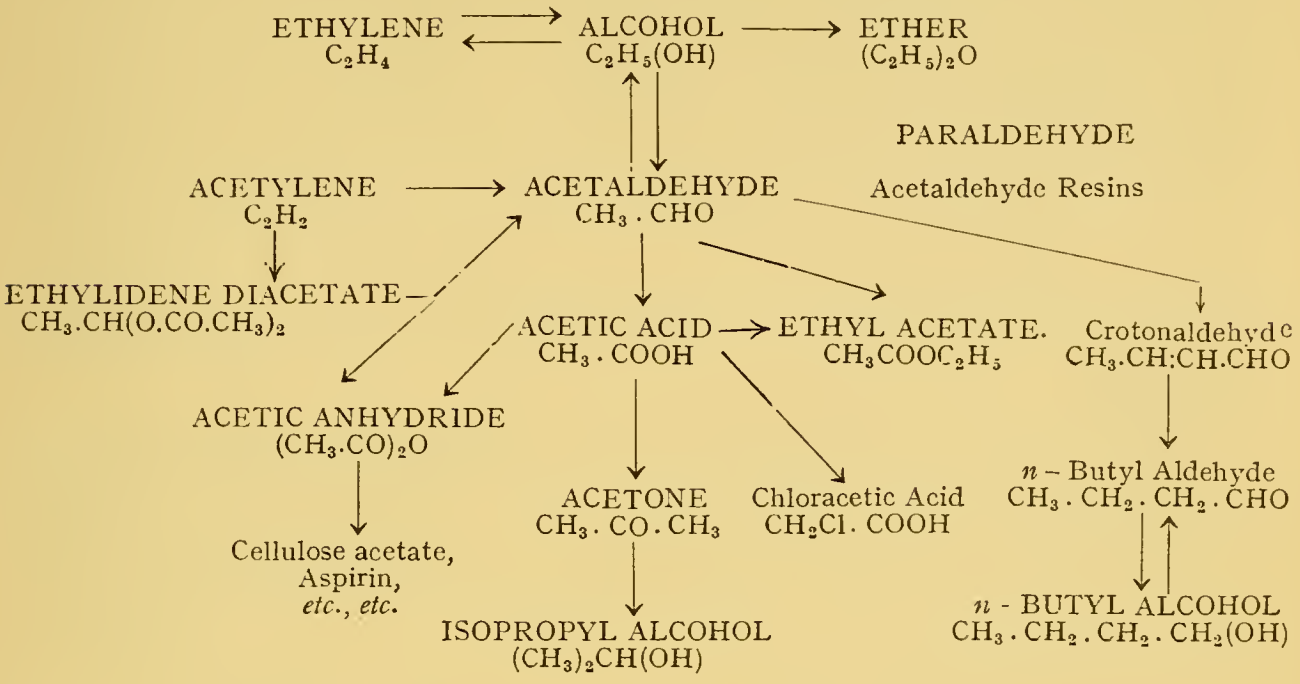
General.—The first patent for the catalytic hydration of acetylene into acetaldehyde appears to have been granted in 1910. Since that date, and owing especially to the stimulus of war conditions in 1915–1916, a very large industry in simple synthetic organic derivatives has been based on the fundamental interaction

$$C_2H_2 + H_2O = CH_3.CHO,$$

which is carried out by the catalytic hydrating action of warm dilute acid solutions of mercuric salts on acetylene.

The Chemische Fabrik Griesheim-Elektron,[1] and others of the large chemical manufacturers in Germany, the Société chimique des Usines du Rhône in France, the Elektrizitätswerk Lonza and the Société de Chimie industrielle de Bâle in Switzerland, the British Cellulose and Chemical Manufacturing Co.[2] in England, the Carbide Industrial Co., Fredrikstad, Norway, and the Canadian Electrochemical Products Co.[3] of Shawinigan, have been prominent in connection with these processes. The last-named company has developed the manufacture of acetaldehyde derivatives on a commanding scale, and is probably at the present time the greatest single producer of acetic acid. In 1919 a production of about 18,000 tons of glacial acetic acid was attained, and this has probably undergone further expansion.

The scope of the acetylene-acetaldehyde industry can be indicated most suitably in diagrammatic form :—



Of the transformations indicated in this scheme, all but a very few are carried out by modern processes of catalysis.

The development of these industries illustrates particularly well the counterplay of economic factors in chemical industry. Synthetic acetic acid has proved a keen competitor for the old glacial acetic acid obtained from wood distillation ; it can be obtained in 99 per cent. purity by a single fractional distillation of the oxidation liquor from acetaldehyde (p. 300), and, with suitable location for the manufacture of carbide, can be produced cheaply and in high yield from acetylene. On the other hand, attempts which have been made in Switzerland and elsewhere to produce industrial alcohol from acetaldehyde do not seem to have yielded the material at rates which compete with fermentation alcohol, in spite of cheap power, acetylene and hydrogen, and of the fact that the reduction process worked efficiently.

Again, synthetic acetone from acetic acid was originally in much demand, and was indeed the first aim of the acetylene-aldehyde process ; contemporane-

ously, however, the *Granulobacter* fermentation of starch (p. 270), yielding acetone and *n*-butyl alcohol, was developed, and fermentation acetone proved to be the more economic form of the product. Nevertheless the demand for butyl alcohol is at present much greater than that for acetone, and in consequence, although little acetone is now made catalytically from acetic acid, considerable quantities of *n*-butyl alcohol are produced from acetaldehyde by the sequence of operations indicated in the above scheme and referred to again below.

The Direct Conversion of Acetylene into Acetaldehyde.—The method described in Matheson's English patent [4] No. 132557 of 1918 may be quoted to illustrate the manner in which this process is carried out in factory practice.

The reaction-vessel, a closed agitator constructed of a silicon-iron alloy and provided with a mechanical stirrer and coils for cooling or heating, is charged with 1,000 gallons of 6 per cent. sulphuric acid to which is added 25 lb. of mercuric oxide. A vigorous current of acetylene (about 60 cubic feet per minute) is passed through the liquid whilst mechanical agitation is applied. The action is exothermic, and is carried on at 60°–65°, mainly by its own heat, cooling being resorted to when necessary ; the system is maintained at atmospheric pressure, except for the back-pressure exerted by the exit acetylene scrubber (up to 2 lb. per square inch). The considerable excess of acetylene present carries away all the acetaldehyde produced, and passes successively through a cold-water condenser, a refrigerated condenser at −10° to −15°, and finally through a cold-water scrubber. The scrubbed gas is pumped back to the reaction-vessel or collected in a storage holder for re-utilisation.

The aldehyde, whether condensed or dissolved in the scrubber-water, is readily rectified by fractional distillation, whilst acetylene dissolved in the scrubber-liquor is simultaneously recovered.

Water is removed from the reaction-vessel both by chemical combination and by evaporation, and this is compensated for by continuous addition of sufficient water to maintain a constant concentration of sulphuric acid in the agitator. Mercuric oxide is also added from time to time to compensate for the slow loss of mercuric salt from the system, by reason of reduction to metallic mercury. At the temperature and acid-concentration selected, side reactions which involve reduction of mercury to the metallic state are probably at a minimum, but they cannot be completely suppressed and a sludge of mercury globules, together with minor amounts of sulphur and phosphorus compounds from the acetylene, slowly accumulates at the bottom of the vessel.

Eventually, also, non-volatile compounds from slight decomposition and polymerisation of the acetaldehyde accumulate to an unwelcome extent in the reaction-liquor, which then has to be replaced by a fresh charge. This condition is only reached, however, after prolonged working, during which period the mercuric oxide has been more or less continuously added to the system and withdrawn in the form of mercury sludge.

The yield of acetaldehyde produced by this process from acetylene is very high and probably approaches 95 per cent. of the theoretical. At the Shawinigan plant of the Canadian Electrochemical Products Company, 500,000–600,000 cubic feet of acetylene were converted per day in 1919 by this process into acetaldehyde.

The accumulated sludge of impure mercury gravitates to the bottom of the reaction-vessels, whence it is periodically withdrawn and passed on, after washing and coagulating as far as possible, into a shallow iron vessel where it forms the anode of an electrolytic circuit and rests beneath a layer of 3–10 per cent. caustic soda solution. It is thus re-transformed into mercuric oxide by anodic oxidation (at a current density of 55 amperes per square foot and 8–10 volts), the

product being removed as formed by a stirrer which sweeps the surface of the metallic mercury.[4]

In the Shawinigan process, therefore, both the raw material (acetylene) and the catalyst (mercuric oxide) are produced by electric power, which replaces all chemicals other than lime and coke for the acetylene, and the minor amount of mercury necessary to compensate for mechanical losses ; thus providing a striking illustration of the efficiency afforded by cheap and abundant electricity in chemical industry.

It may be added that the earlier patents of the Chemische-Fabrik Griesheim-Elektron,[1] the Consortium für Elektrochemische Industrie,[1] and other continental firms, indicate a wide range of temperature and concentration of acid, the earliest disclosure (E.P. 29073/1910) advocating the use of 45 per cent. sulphuric acid or 25 per cent. phosphoric acid. It was observed that the higher concentrations of acid tended to retard the reduction of the mercuric salt present, but, of course, increased the loss of aldehyde due to polymerisation and resinification. Prior to the appearance of the Shawinigan patents [4] the general tendency was to recommend the use of more dilute mineral acid [5] (or, for example, of acetic acid containing a small amount of sulphuric acid) coupled with a moderate temperature, *e.g.*, between 55° and 70°.

The milder mineral acid conditions conduced to higher yields of acetaldehyde and less fouling of the reaction solution with organic by-products, whilst suggestions were made to prolong the life of the mercuric salt by addition of suitable oxidants. Thus, Meister, Lucius and Brüning [6] observed that the presence of ferric salts or of chromic acid increased the amount of aldehyde producible by unit weight of mercuric salt, whilst Crosfield's and Hilditch [7] showed that periodical addition of hydrogen peroxide, peracids or peroxides, such as manganese dioxide, lead dioxide, etc., to the spent reaction-liquor reconverted the mercury present to the active mercuric salt.

Undoubtedly, however, this process is most effectively carried out, as already stated, under conditions where a natural supply of cheap electric power is available, in place of catalyst recuperation by chemical methods.

The Conversion of Acetylene into Ethylidene Diacetate.—If glacial acetic acid is employed in place of aqueous mineral acid in the foregoing interaction, the product obtained is the diacetate of ethylidene glycol (or acetaldehydrol). The former process may be regarded as the hydration of acetylene :—

$$CH : CH + \begin{matrix} H.OH \\ H.OH \end{matrix} = CH_3.CH(OH)_2 = CH_3.CHO + H_2O,$$

and in presence of acetic acid instantaneous esterification of the unstable aldehydrol may be supposed to occur :—

$$CH : CH + \begin{matrix} H.OH \\ H.OH \end{matrix} + 2CH_3.COOH = CH_3.CH(OH)_2 +$$

$$2CH_3 . COOH = CH_3.CH(O.CO.CH_3)_2 + 2H_2O$$

or, summarised :—

$$CH : CH + 2CH_3.COOH = CH_3.CH(O.CO.CH_3)_2.$$

At first sight this is a complication of the alternative synthesis of acetaldehyde, but its importance lies in the fact that ethylidene diacetate can be readily decomposed into acetic anhydride and acetaldehyde :

$$CH_3.CH(O.CO.CH_3)_2 = CH_3.CHO + O(CO.CH_3)_2.$$

This method, therefore, provides a means for producing acetic anhydride from acetic acid, whilst in the same sequence of actions acetylene is converted into acetaldehyde, which serves by oxidation to yield fresh quantities of acetic acid. Since acetic anhydride is required in large quantities, this relatively simple means of production is sufficiently attractive to make it of considerable technical importance.

The earlier patents dealing with this reaction were mainly due to Boiteau [8] and the Société chimique des

Usines du Rhône,[9] whilst later improvements [10] have been protected by the other large concerns operating in this field.

The technical procedure is similar to that in the conversion of acetylene into acetaldehyde, the aqueous sulphuric acid being replaced by a charge of anhydrous acetic acid, to which is added a small percentage of mercuric acetate and about 2 per cent. of sulphuric acid. The action is carried on until absorption of acetylene by the acetic acid falls off considerably, and the product is then decomposed by heat in presence of a suitable catalyst.

The latter decomposition is aided by the presence of small quantities of anhydrous salts or acids of a dehydrating nature; zinc chloride, sodium pyrophosphate, boric acid or sulphuric acid have been proposed for this purpose. The distillation is best effected at a low pressure (*e.g.*, 100 mm.) and a temperature not exceeding about 80°, whilst it is also stated that by heating the ethylidene diacetate at about 125°–135° at atmospheric pressure in presence of acid salts, such as pyrophosphates, or with granulated zinc, almost quantitative resolution into acetaldehyde and acetic anhydride can be obtained.

If a strong acid such as sulphuric acid is used at this stage, the acetaldehyde may be largely polymerised into paraldehyde, a derivative which is used to a considerable extent in medicine.

Products Derived from Acetaldehyde.

We will deal in the next place with materials of technical value which are produced at the present time from synthetic acetaldehyde. Whilst attention must be concentrated upon those compounds which are obtained from the aldehyde by the application of further catalytic methods, it is proposed to make the list as complete as possible, independently of whether subsequent treatment of the acetaldehyde is by catalytic means or otherwise.

Three classes of products may be distinguished :—

(*a*) *Polymerised or condensation derivatives of acetaldehyde* (paraldehyde, acetaldehyde resins, ethyl acetate and crotonaldehyde) ;

(*b*) *Reduction products* (ethyl alcohol and its derivatives) ;

(*c*) *Oxidation products* (acetic acid and its derivatives).

(*a*) *Polymerised or Condensation Derivatives of Acetaldehyde.—Paraldehyde*[11] is the trimolecular form of acetaldehyde $(C_2H_4O)_3$, and is a liquid of characteristic odour which boils at 124°. It has an extended use in medicine as a powerful sleep-inducing and sedative agent, whilst suggestions have been put forward recently for its use, in conjunction with alcohol or petrol, as a motor fuel.

Acetaldehyde is readily transformed into the trimolecular polymeride in presence of small quantities of strong acids. Simple contact with minute amounts of concentrated hydrochloric acid causes acetaldehyde to pass into paraldehyde with considerable evolution of heat. The action is conveniently carried out by agitation of acetaldehyde, in a cooled vessel with a good condenser, with successive additions of a few drops of the concentrated acid, until further addition causes no liberation of heat. The action is an equilibriated one, and when a final state of balance is reached the mineral acid is exactly neutralised with bicarbonate (in order to avoid any aldol condensation) and the mixture is fractionally distilled, when unchanged aldehyde is first recovered and subsequently the paraldehyde which has been formed distils over.

Acetaldehyde resins[12] may next be mentioned ; it has been found that acetaldehyde, as well as formaldehyde, is capable of condensation with phenols, the products being complex, difficultly-fusible or insoluble resins of a similar nature to the well-known phenol-formaldehyde or Bakelite compounds. Whether such acetaldehyde resins are in every respect equally

serviceable with the formaldehyde products does not appear yet to be conclusively settled, but patents have been taken out for their production from phenols and either acetaldehyde itself or paraldehyde, usually by means of condensation in presence of a mineral acid.

Ethyl acetate[13] (*cf.* also p. 322) can be produced directly from acetaldehyde in very high yields by what is essentially a polymerisation process :—

$$2CH_3.CHO = CH_3.COOC_2H_5.$$

This action, which recalls the conversion of benzaldehyde into benzyl alcohol and benzoic acid in presence of caustic potash :

$$2C_6H_5.CHO = C_6H_5.COOH + C_6H_5.CH_2.OH,$$

or into benzyl benzoate by means of sodium (*cf.* p. 323), is effected by means of small proportions of aluminium ethylate. The ethylate alone does not produce a very high conversion of aldehyde into ester, but if anhydrous aluminium chloride is also present the conversion usually exceeds 90 per cent. A recent patent[13a] advises that a mixture of anhydrous aluminium chloride and aluminium powder be refluxed with alcohol and ethyl acetate until the metal present has been transformed into alcoholate with evolution of hydrogen. The resulting liquid, which contains aluminium chloroethylates, is then well cooled and acetaldehyde is run in with vigorous stirring and cooling until, for example, the aluminium derivatives present form only about 5 per cent. or less of the whole. The aldehyde is rapidly transformed into ethyl acetate, which is purified by fractional distillation.

This polymerisation affords the most direct synthesis of ethyl acetate (which is, of course, an important solvent and fine chemical) from acetylene *via* acetaldehyde.

Although not at present used to this end, it should also be borne in mind that the process represents a dual synthesis of ethyl alcohol and acetic acid from acetylene,

capable of technical application if circumstances warranted the use of the method.

Crotonaldehyde represents a further type of intermolecular condensation of acetaldehyde which is of technical importance as a link in the commercial synthesis of butyl alcohol from acetylene :—

$$2C_2H_2 \longrightarrow 2CH_3.CHO \longrightarrow CH_3.CH : CH.CHO \longrightarrow CH_3.CH_2.CH_2.CH_2(OH).$$

Crotonaldehyde, or rather its predecessor aldol $CH_3.CH(OH).CH_2.CHO$, is produced by the action of mild alkaline agents on acetaldehyde, excess of alkali or the use of too caustic an alkali leading to the formation of large proportions of sticky, semi-solid complex aldehydic resins. It has been proposed, for example, to treat the acetaldehyde with strontium oxide, whilst baryta or lime are probably effective under controlled conditions. The crude condensation product, on distillation at ordinary pressure in a current of inert gas, first of all yields unchanged acetaldehyde and then, at a somewhat elevated temperature, the aldol breaks up into water and crotonaldehyde :—

$$CH_3.CH(OH).CH_2.CHO = H_2O + CH_3.CH : CH.CHO.$$

The latter is hydrogenated, in either the vapour or the liquid state, by means of nickel according to the methods described in Section II. (pp. 181, 208), when the ethylenic linkage is saturated and the aldehydic radicle reduced to a primary alcoholic group.

As already stated, butyl alcohol is in increasing demand as a solvent, especially for modern lacquers and spirit varnishes, and the above synthesis from acetylene by a sequence of catalytic actions is applied on a considerable technical scale at the present time.

(*b*) *Reduction Products of Acetaldehyde.*—It has not yet been proved to be economical, although it is technically feasible, to manufacture ethyl alcohol by the hydrogenation of acetaldehyde. At the same time, as the process in question has been thoroughly tested on the large scale, it is reasonable to say that, starting from

carbide or acetylene, it is practicable to effect the large-scale production of ethyl alcohol and therefore, of course, the wide variety of compounds (ethylene, ether, ethyl esters, etc.) of which alcohol is the starting-point.

The hydrogenation of acetaldehyde has been carried out by modifications of the original Sabatier[14] vapour process as described in Section II., Chapter VII (p. 182). Large-scale operations by the Elektrizitätswerk Lonza,[15] in Switzerland, with the full advantages of cheap water-power and electrolytic hydrogen, have proved technically successful, but the costs involved do not appear at present to render the process a competitive one. The hydrogenation is conducted in presence of a large local excess of hydrogen, and the latter contains 0·3 per cent. of oxygen. The object of the added oxgyen is to restrain the formation of ether, whilst the large excess of hydrogen is designed to absorb or remove the heat developed in the hydrogenation as rapidly as possible, so that aldehyde is not lost by pyrogenetic decomposition. For the same reason, the temperature of the system is not allowed to rise above 150°. Reduced nickel is employed as catalyst.

It has been estimated that, assuming yields of 80, 90 and 90 per cent. in the three phases, carbide to acetylene, acetylene to aldehyde, aldehyde to alcohol, one ton of alcohol should result from two tons of crude carbide, and that the total cost of one ton of alcohol might not exceed the following :—

	£
Carbide (2 tons at £8 per ton)	16·0
Conversion to acetaldehyde	3·5
Hydrogenation to alcohol (including 20,000 cub. ft. electrolytic hydrogen)	6·5
	£26.0

or an approximate cost of 2*s*. per gallon of alcohol.[16]

The economically successful operation of this process

rests, apparently, therefore, on the relative cost on the one hand of calcium carbide and on the other of grain or cellulose material suitable for conversion into alcohol by fermentation; and it seems likely that, other than in exceptional localities, the balance will remain in favour of fermentation processes, at all events in the immediate future.

(*c*) *Oxidation Products of Acetaldehyde*.[17]—Probably most of the acetaldehyde synthesised technically from acetylene is at once converted into acetic acid by oxidation, and the process about to be described follows immediately after acetaldehyde resulting from the methods dealt with on pp. 290–294 has been rectified by distillation. Although, therefore, a digression has been made above in order to discuss the condensation and reduction products of the aldehyde, most of the latter is submitted in actual practice to an oxidation process which belongs to the class of catalysis in homogeneous systems which is now under consideration.

Acetaldehyde is converted by simple passage of a current of oxygen or air into acetic acid, in presence of catalysts which consist of the acetates of certain metals of high and variable valency, notably manganese. The catalyst, however, does not in this case appreciably accelerate the first product formed in the action, for acetaldehyde, if sufficiently pure and dry, absorbs oxygen smoothly and steadily with formation of the highly unstable peracetic acid, or acetyl peroxide:

$$CH_3.CHO + O_2 = CH_3.CO.O.OH.$$

This compound, when obtained in a concentrated condition, is exceedingly explosive and, moreover, sudden decomposition of a relatively small amount will detonate a mixture of acetaldehyde vapour and oxygen; it is therefore essential to keep the concentration of peracetic acid in the charge as low as possible, and certainly of the order of not more than 1 per cent. of the whole, whilst precautions are taken

to prevent condensation of peracetic acid vapour in any isolated parts of the vessel or connections. The main function of the " catalyst " is to effect continuous and smooth decomposition of peracetic acid as formed, a result which is also aided by the use of as high a temperature as is consistent with the vapour tension of acetaldehyde and the pressure which it is safe to employ. In the earlier stages of the process, when acetaldehyde is present in large proportions, this should not exceed 30 lb. per sq. in., but towards the end, so long as practically complete absorption of oxygen (*i.e.*, absence of oxygen in the gaseous phase above the liquid) persists, the pressure is frequently allowed to rise to 60–75 lb. per sq. in.

In presence of manganese acetate the onset of the reaction is marked by development of a deep brown coloration—the manganese present is transformed by the peracetic acid into a higher state of oxidation :—

$$y\mathrm{CH_3.CO.O.OH} + x\mathrm{MnO} = y\mathrm{CH_3.COOH} + \mathrm{Mn}_x\mathrm{O}_{x+y}.$$

The higher oxide is reduced immediately by more acetaldehyde :—

$$\mathrm{Mn}_x\mathrm{O}_{x+y} + y\mathrm{CH_3.CHO} = y\mathrm{CH_3.COOH} + x\mathrm{MnO}.$$

and the regenerated manganous salt is ready to reduce more peracetic acid. The catalyst must be present in the form of an organic salt which is comparatively soluble in acetaldehyde.

As already mentioned, pure dry acetaldehyde is capable of immediate absorption of oxygen, but it is necessary to observe these conditions, otherwise little or no action takes place except in the gas phase above the liquid and in these circumstances there is some risk of explosion. Normally, however, the process proceeds rapidly and smoothly in the liquid phase until nearly all aldehyde has been oxidised to acetic acid.

The crude acid is dark brown in colour, owing to the oxidised manganese salt present and to the formation of a minor amount of dark-coloured resinous impurities

(less than 1 per cent. of the product). It is purified by distillation through a fractionating column, one distillation usually yielding an almost colourless acid of 98–99 per cent. purity. The ease with which a "glacial" acetic acid can be produced from the crude product gives the synthetic process a marked advantage over the older process of recovery of acetic acid from wood-distillation acetates of lime.

The working details of the catalytic oxidation of acetaldehyde may be gathered from the following abstract of Matheson's English patent:[18] A closed vessel with suitable resistant lining, *e.g.*, of aluminium, is provided with coils through which water or steam may be passed. An air-pipe is provided, extending to the bottom of the vessel, where it is arranged in spiral form with a multitude of small openings, so that the air is finely distributed over the whole area of the vessel. The vessel is charged with 1,000 gallons of acetaldehyde and about 0·5 per cent. of manganese acetate or other catalyst. Steam or warm water is passed through the coils to raise the temperature to 20°–25°, and air is admitted at a rate of up to 300 cub. ft. per minute. The oxidation takes place with evolution of heat, which is controlled by passing cold water through the coils. The temperature is always maintained not much below the boiling point of the aldehyde under the pressure used, and after the action commences, the pressure is allowed to rise slowly to about 75 lb. per sq. in., and the temperature to 65°. Under these conditions the absorption of the oxygen is complete and the nitrogen is allowed to escape through a relief valve after passing through a cold-water condenser at 1°–5°, and a brine condenser at — 10° to — 15°, each of these being under the same pressure as the reaction vessel. The condensed liquid returns to the reaction vessel through U-seals, and the escaping nitrogen is passed through a scrubber supplied with water at 0°, and maintained at a pressure of 20 lb. per square inch. The reaction is complete

in eight to eighteen hours, after which the contents of the vessel are discharged and the acetic acid is purified by distillation.

As already stated, about 18,000 tons per annum of acetic acid were already being produced in 1919 at Shawinigan by this process.

Products Derived from Synthetic Acetic Acid.

Acetic acid is required in large quantities as such, in the form of metallic salts, especially those of sodium, iron, aluminium and lead, and in its many esters which find employment as drugs, perfumes, essences, or solvents (the direct technical production of *ethyl acetate* from acetaldehyde has already been noticed (p. 296)).

Attention is more particularly directed here to those derivatives of the acid which are largely used in technology, especially in the industries of artificial silk, explosives, lacquers and perfumes.

Acetic Anhydride, together with the acid, is needed in immense quantities in the manufacture of acetyl-cellulose, and for other acetylated products of which the dyestuffs industry and the fine chemical industry (*e.g.*, aspirin and phenacetin) afford many examples. Whilst it is still prepared in quantity by the older methods of the action of sulphuryl (or phosphoryl) chloride on sodium acetate, increasing amounts are produced from ethylidene diacetate (*cf.* p. 293), the latter being synthesised from acetylene and synthetic acetic acid.

Chloracetic Acid (see also p. 340), obtained by chlorination of acetic acid, is an important intermediate in the production of synthetic indigo ; an alternative proposal for its manufacture consists in the action of sulphuric acid at 160°–190° on trichlorethylene :—

$$CH_2Cl.CHCl_2 + 2H_2O = CH_2Cl.COOH + 2HCl.$$

Acetone is needed in large quantities as solvent and for other purposes. As already stated, fermentation acetone (with wood-distillation acetone) holds the field

at the moment, but it has been manufactured from acetic acid both in Europe and America by catalytic decomposition of the acid vapours in presence of alumina or lime, as described in Section II., Chapter VIII (p. 193). The process as used at Shawinigan consisted in passing the pre-heated vapours of synthetic glacial acetic acid through steel tubes, 13 ft. long and 1 ft. in diameter, containing hydrated lime mixed with a small quantity of magnesia coated on to rough cast-iron balls. At 483°, 95 per cent. of the acid was converted into acetone; the vapours from the tubes were scrubbed in a soda-tower, and the aqueous acetone was then rectified in a continuous still.

Isopropyl Alcohol may be quoted as a final instance of the products obtainable from acetylene by modern synthetic catalytic methods. Used in increasing quantities as a substitute for ethyl alcohol in perfume essences and similar materials, it is prepared by catalytic hydrogenation of acetone according to the methods of which an account has already been given (Section II., Chapter VII, p. 183).

The Production of Ethyl Alcohol from Ethylene.[19]

The olefine gases, of which ethylene is the most common and important, are not met with in technology to the same extent as acetylene, but they are present in fairly large amounts in several industrial gases, and it is probable that the latter will find increasing use as sources of ethylene and, perhaps to a less extent, of higher olefines. Ethylene, for example, can be transformed into a number of useful aliphatic products; it can be readily made to combine with chlorine, when useful solvents result, or with hypochlorous acid, forming ethylene chlorhydrin. Both of these products can be further acted upon, with the result that a way is opened for the manufacture of ethylene glycol and its derivatives (*e.g.*, the dinitrate) from ethylene. Processes of these types (which, not involving catalytic action, are strictly outside the pro-

vince of this volume) are already in operation in America and elsewhere; a process of a semi-catalytic nature which deserves mention here, however, is the conversion of olefines into alcohols by absorption in concentrated sulphuric acid.

Before describing this, it may be stated that the chief sources of cheap ethylene (accompanied by smaller proportions of propylene, butylenes and amylenes) are as follows :—

(*a*) The "natural gas" which escapes in large quantities from many of the oil-bearing strata of America and elsewhere ;

(*b*) "Cracked gas," that is, the mixture of gaseous hydrocarbons and hydrogen produced when heavy petroleum oil is submitted to pyrogenetic decomposition in the manufacture of "cracked" petrol spirit—a very large industry ;

(*c*) Coke-oven gas—the gaseous compounds produced in the distillation of coal for various purposes, for example, producer-gas, illuminating gas, or for metallurgical coke.

The production of alcohol from ethylene by absorption in sulphuric acid

$$\begin{cases} C_2H_4 + H_2SO_4 = C_2H_5.HSO_4 \\ C_2H_5.HSO_4 + H_2O = C_2H_5OH + H_2SO_4 \end{cases}$$

has been studied exhaustively on the large scale, but it does not appear that alcohol is made industrially at present in any great amount by this process. An account of work carried out at the Skinningrove Iron and Steel Company's works, North Yorkshire, indicates that coke-oven gases containing about 1·7–1·8 per cent. of ethylene (after scrubbing in 80 per cent. sulphuric acid to remove moisture and higher olefines) can be absorbed efficiently in sulphuric acid of 95 per cent. strength at 80°–85°. Above this temperature carbonisation of the organic compounds and formation of sulphur dioxide sets in. In a tower scrubber 18 per cent. of the sulphuric acid present can be combined

with ethylene, but if further scrubbing of the gas in a mechanically-agitated washer supervenes, the conversion is considerably higher. The absorption is accelerated in presence of silica.

Acid of higher concentration than 95 per cent. causes diethyl sulphate and even carbyl sulphate to be produced.

In order to obtain the free alcohol, the spent acid is diluted with water to 64 per cent. concentration and then distilled under reduced pressure (at 94°–146°). The residual acid (which is free from alcohol) is then of 80 per cent. strength.

The experiments indicate that an alcohol plant to deal with the coke-oven gases from a carbonisation of 800 tons per day would require the use of nine towers 10 ft. diam. and 80 ft. high; if 70 per cent. of the ethylene were absorbed and, of this, 70 per cent. were recovered as alcohol, the daily production of the latter would be about four tons.

Put in another way, it is estimated that 1·6 gallons of absolute alcohol could be obtained from each ton of coal carbonised, equivalent to a total possible annual production of 59,000,000 gallons of alcohol from the 37,000,000 tons of coal carbonised in gasworks and coke-ovens in this country; obviously, owing to the elaborate installation necessary and for other reasons, the practical output could only be a fraction of the total amount potentially available.

Damiens[20] has observed that sulphates of various metals, notably cuprous sulphate, stimulate the absorption process.

In order to produce diethylsulphate (required to some extent in the dye and fine chemical industries for ethylation), Curme[21] has proposed to conduct the absorption in more concentrated sulphuric acid.

Finally, a group of American chemists[22] connected with the Standard Oil Company, has accomplished considerable work on this problem and has found that the presence of mineral oil with the sul-

phuric acid leads to more efficient fixation of the ethylene ; they also report the successful production and isolation on a commercial scale of the secondary propyl, butyl, amyl and hexyl alcohols (of the general formula $CH_3.CH(OH).[CH_2]_n.CH_3$) from propylene, butylene, amylene and hexylene present in " cracked gas."

It has been mentioned earlier in this chapter that isopropyl alcohol is used in perfumery and for other purposes ; secondary butyl alcohol can be converted into methylethylketone by dehydrogenation (*cf.* p. 181), whilst this alcohol and the corresponding amyl and hexyl compounds are useful as solvents and to a smaller extent for synthetic purposes.

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CHAPTER II

ACTIONS OF HYDROLYSIS IN LIQUID SYSTEMS

The production of esters from an acid and excess of alcohol is greatly accelerated (and the conversion increased) in presence of small concentrations of strong acids, and similarly the latter catalyse the resolution of an ester in presence of excess of water into its component acid and alcohol.

This is usually attributed to the catalytic (hydrolytic) action of the hydrogen ion, so far as hydrolysis in an aqueous solution is concerned :—

$$R.COOR' + H_2O = R.COOH + R'.OH.$$

In general technical practice, the use of acid hydrolysis of a simple ester is rarely employed, for in the majority of cases the manufacturer is concerned to synthesise, not to break up, an ester ; and, as this reaction has already received theoretical treatment in Section I (pp. 53, 56), no purpose will be served here by enlarging further on the practical details involved.

The principle in question is applied technically, however, in the acid hydrolysis of natural complex carbohydrates, when simple hexose sugars are produced ; and some account of the technical conversion of starch and cellulose material into sugars by means of acids is therefore necessary.

Such transformations are also carried out to a great extent in industry in the course of processes of fermentation, for example, the production of alcohol from malt or from molasses ; these hydrolytic actions, and also the lipase hydrolysis of fats, have already been considered in Section III. from the general standpoint of catalysis by enzyme action.

There remain two or three other important instances

of technical hydrolytic actions accelerated by non-enzymic or ordinary catalytic agents, which will be quoted as further examples of the industrial applications of catalysis in this field. Firstly, we have three independent methods (each of which is employed to a very wide extent) for the hydrolysis of that important class of esters, the fats ; and, in the next place, the commercial production of benzaldehyde and benzoic acid from chlorinated toluene (benzalchloride and benzotrichloride) deserves consideration as an example of this type of process.

Conversion of Starch into Simple Carbohydrates by Mineral Acids.[1]

This process has a two-fold importance ; it has been employed for a long time in the manufacture of glucose for sweetening and edible purposes, and it has also been used, and will probably be used on a larger scale still, for the conversion of starches into readily-fermentable products. Chemically the two aspects of the industry are the same, but in the latter case the final objective is not a crystalline sugar or sugar syrup, but a solution which can be fermented to yield alcohol for potable, industrial, or fuel and power purposes.

Manufacture of Crystalline Glucose or of Sugar Syrup.—The raw materials subjected to the process vary according to the country ; thus in England, rice, sago, maize and potatoes are used, in Germany mainly potatoes, and in North America maize is by far the most common starting-point. The acids employed also vary according to local conditions and, whilst hydrochloric acid is most generally used in the United States, sulphuric acid is the usual medium in England.

The process is purely catalytic and dependent on the hydrogen ion concentration of the system ; the actual proportion of aqueous acid to starch has little influence on its course. The ultimate desired action is summarised in the equation

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6,$$

but this by no means depicts what actually takes place. The first products of degradation of the starch are dextrins and maltose, whilst glucose is probably also present from the commencement of hydrolysis.

Dextrins are carbohydrates intermediate in complexity between disaccharides, such as maltose, and starch or cellulose, and probably comprise about four hexose units condensed together in the dextrin unit. Like disaccharides, they are freely soluble in water, but, unlike these, are insoluble in 70 per cent. alcohol; whilst disaccharides do not react with iodine, dextrins give a reddish-brown colour in place of the familiar deep blue-black colour given by starches.

Maltose is a disaccharide made up of two condensed molecules of glucose, and further action of the acid, either on dextrin or maltose, produces glucose; glucose itself is slowly attacked by the mineral acid if the concentration of the latter or the time of contact be too great.

The conversion, as a matter of fact, proceeds very rapidly. Formerly, it was carried out in open, lead-lined wooden converters with a 5 per cent. solution of sulphuric acid in water, two parts of starch being mixed with five parts of the aqueous acid solution; complete conversion to glucose by this means requires treatment for four or five hours. In modern factories the operation is usually effected in closed converters of copper or gun-metal under a steam-pressure of from 10–30 lb. per sq. in. *i.e.*, at about 110°–125°. The acid concentration necessary is then only 0·5–0·6 per cent., and complete hydrolysis to glucose takes place in about one and a half hours. In the latter case the liquor is tested with iodine until the absence of the reddish-brown tint shows that dextrin has disappeared, but in order to produce sugar syrup (syrup of glucose, corn syrup) partial hydrolysis only is effected, and the carbohydrates present in the finished syrup consist of about equal proportions of dextrin and glucose with about 20 per cent. of water, the hydro-

lytic action only occupying thirty to fifty minutes as a rule.

The acid liquor is nearly neutralised with carbonate of lime (sulphuric acid) or soda-ash (hydrochloric acid), settled and filtered ; the filtrates are evaporated to a certain extent, passed through decolorising charcoal (char) and further concentrated in a vacuum evaporator to syrup of the desired moisture content, or to crystallisation, as the case may be. In the latter case crystalline glucose is separated by cooling and centrifuging.

Conversion of Starch Materials into Fermentable Sugars.—The technique of this process is the same as that given above, but the raw material employed depends on local and other conditions. For potable alcohol, and also for industrial alcohol, rice-starch and potato-starch are used in Europe and also, together with maize, in America. It is stated by the Department of Scientific and Industrial Research that more suitable home sources of fermentable sugars for industrial and power alcohol would probably be mangolds and Jerusalem artichokes. In the Dominions and India other suitable sources of starch include cassava, sweet potatoes, arrowroot, etc., as well as rice and maize.

Conversion of Cellulose into Fermentable Sugars by Mineral Acids.

The degradation of the cellulose system into its component monosaccharides is unfortunately much more difficult to achieve completely than that of starch. Vast quantities of cellulose occur in nature in the form of practically useless material, for example, the abundant grasses of the tropics, Australia and South America, the straw of maize, rice and other cereals, the chaff or husks of many seeds, cotton-seed hulls, maize cobs, etc., etc., and sawdust and waste small wood from cut timber.

The dilute acid process referred to above has a

certain effect on cellulose material, and is employed to an increasing extent in North America and elsewhere ; but whilst, expressed in terms of final yield of alcohol, one ton of starch gives a practical output of 80 gallons of 95 per cent. alcohol, one ton of cellulose yields only 20–25 gallons of the spirit in practice. The reason for this is that cellulose material is composed of three types of complex carbohydrate material, cellulose, lignocellulose and hemicellulose, and only the latter is readily hydrolysed by dilute aqueous acid. The proportion of hemicellulose present is usually about 25–40 per cent., and it is this part of the whole fibre which is convertible into monosaccharides. Of the latter, a considerable proportion, depending on the species of the original plant, may be pentoses (xylose) and not the yeast-fermentable hexose glucose, but in such cases processes are available (*cf.* Section III., pp. 275–278) for fermentation by means of appropriate bacterial cultures, which produce ethyl alcohol with, in some cases, acetone as a secondary product.

The manipulation of the dilute acid hydrolysis is much the same as in the case of starch, but the action proceeds at a slower rate. Working under pressure and at a concentration of about 0·6 per cent. sulphuric acid, about four or five hours is required ; whilst with 2 per cent. acid at atmospheric pressure the operation takes at least seven hours.

A useful modification of the method, economising space and volume of aqueous acid used, consists in soaking the dried wood waste with acid of 1–2 per cent. strength, when the cellulose material will take up at least its own weight of liquid and still remain dry enough to handle. It is then either steamed at atmospheric pressure or passed through a steam-jacketed worm conveyor, where it is heated externally by steam at 80–100 lb. per sq. in. pressure.

In either case the finished product still contains at least 70 per cent. of insoluble cellulose, and the soluble portion is extracted in diffusion batteries similar to

those used in the beet-sugar industry. The further treatment of the aqueous extract prior to fermentation is the same as in the case of the starch processes.

Much research has been undertaken in order to convert the more refractory constituents of cellulose into soluble sugars, and it appears probable that the employment of concentrated or gaseous hydrochloric acid in place of dilute aqueous acid effects the desired hydrolysis and permits of the production of 80 gallons of industrial alcohol per ton of cellulose material.[2] The practical difficulties involved in the large-scale application of this process are evidently formidable, but there is little doubt that they will be surmounted in due course.

The primary incentive to applied research in this field is, of course, the desirability of producing power alcohol on a large and economic scale, but it should be borne in mind that, apart from this main object, the production of sugars of various types *per se* is of possible commercial interest, although at present of subsidiary importance.

Whilst dealing with the subject of cellulose degradation, passing reference may be made to the presence of sugars in the waste liquor from the sulphite process for the conversion of cellulose into paper; these liquors, which, after suitable treatment, are fermentable, correspond in character with the aqueous extracts produced by the above acid processes.

Hydrolysis of Fats.

When fats are to be converted into soaps, it is usually most economical to hydrolyse them directly with aqueous soda (or potash), thus at once producing the soda (or potash) soaps, which are ready, after washing and cleansing, for mechanical transformation into bars, tablets, powders, or other form in which they pass into the market.

When the fatty acids are required as such for other purposes, for example, candle manufacture or leather-

dressing, the saponification process, followed by liberation of the free acids by mineral acid, is somewhat cumbersome. Moreover, it is evident that the expense of caustic soda could be avoided if water alone were employed as hydrolytic agent; and, even for soap-making, caustic soda could thus be replaced by the cheaper soda-ash, which would be used subsequently to neutralise the liberated fatty acids. Also, since concentration and recovery of the glycerine simultaneously set free from the fats is an important economic feature of fat-hydrolysis, processes which lead to the formation of a comparatively concentrated glycerine liquor (*e.g.*, 15–16 per cent. glycerine) have an important advantage in this respect over the ordinary saponification, in which the lyes usually contain only 3–5 per cent. of glycerine.

Fats can be hydrolysed by water alone, but the temperature necessary (200°–220°) before the action proceeds at a technically useful speed is too high for economical working, involves an equivalent steam pressure of nearly 250 lb. per square inch, and leads to serious discoloration of the fatty acids produced. Certain basic oxides, however, exert a powerful catalytic effect on the rate of hydrolysis, and complex fatty-aromatic sulphonic acid derivatives known as the *Twitchell hydrolytic agent* are equally serviceable as catalysts in the splitting of fats, whilst sulphuric acid alone is a useful fat-splitting agent in the case of very crude materials. All these methods, and also the lipase fermentation process which has already been referred to under *Fermentation* in Section III. (p. 281) are employed on the large scale in the production of fatty acids, and are instances of technical hydrolysis promoted by catalytic means.

The Autoclave Process of Fat-hydrolysis.—Hydrolysis in presence of basic oxides (especially lime, magnesium and zinc oxide) is termed in works practice the "autoclave process," owing to the action being carried out in pressure-agitators at about 140°–150° (100–120

lb. per square inch steam pressure). This process is in fairly wide use, more especially when the fatty acids themselves are the objective, and it can be completed in the same time as that necessary at 250 lb. per square inch pressure of steam in the absence of the catalytic bases. It is carried out in stout vertical cylindrical vessels with dished ends, steam-jacketed or fitted with an internal closed coil; sometimes mechanical stirring is used; more frequently agitation is effected by a current of steam, distributed into the lower part of the vessel by a perforated pipe and maintained by the continuous withdrawal of a certain amount of steam from the head of the vessel.

The autoclave is charged to about 70–80 per cent. of its capacity with a mixture of about 80 parts of fat and 20 parts of water, together with about 3 parts of lime, or a mixture of lime and zinc dust. (The zinc dust, which contains both metallic zinc and oxide, serves as a catalyst and also aids in preserving the acids from undue discoloration; the latter function is probably due to the reducing action of the metallic zinc present.) The concentration of basic oxide which experience has shown to be desirable is abnormally high for a strictly catalytic operation, and is about 30 per cent. of that necessary to neutralise the total fatty acid produced.

The autoclave is kept at a pressure of 100–120 lb. per square inch for ten or twelve hours, during which hydrolysis proceeds, according to the law of mass action, at a rate which is governed by the amount of unsaponified fat present. Thus 90 per cent. of the fat is usually hydrolysed in from three to five hours, but conversion of 98–99 per cent. of the fat to fatty acids requires, as stated, ten to twelve hours. When the latter stage has been reached the contents of the autoclave are blown into a wood-lined tank (well lagged externally), in which they can settle slowly while still warm. After some hours the lower layer of aqueous liquor (" sweet water "), which may

contain up to about 15 per cent. of glycerine, is drawn off for evaporation to crude glycerine; the upper layer of fatty acid and lime soap is boiled up by means of steam, sufficient dilute sulphuric acid is added to neutralise the lime present, and the fatty acids are settled and finally washed by further boiling with water.

The Twitchell Process of Fat-hydrolysis.—In 1900, Twitchell [3] published details of a catalyst or "emulsifying agent" by means of which fats could be completely hydrolysed by water below 100°. The agent in question was prepared by treating a mixture of oleic acid and benzene or, better, naphthalene, with concentrated sulphuric acid; sulphonation and condensation took place, the resulting product (when naphthalene was employed) being apparently of the general formula, $COOH.C_{17}H_{34}.(C_{10}H_6).SO_3H$.

The agent, after being washed free from sulphuric acid, is employed in about $\frac{1}{2}$–1 per cent. concentration on the fat to be hydrolysed.

The process is carried out in a wooden vat with a loose lid, fitted with a perforated copper coil for the admission of steam. The fat, which should have been clarified previously by boiling with dilute sulphuric acid and settling, is run in, together with about 50–100 per cent. of its weight of water, and the Twitchell agent in the proportions stated. The mixture is maintained in a state of gentle ebullition throughout the process by a current of steam from the open coil. After a period of induction, hydrolysis sets in fairly rapidly, the rate declining steadily as the concentration of neutral fat diminishes; the process usually takes from one to three days for completion. Time is saved by interrupting the charge when it is about half-hydrolysed, settling and drawing off as much aqueous glycerine as possible, adding more water to replace that withdrawn and resuming the operation.

A conversion of 97–98 per cent. of the fat to fatty acids is usually reached before the latter are worked up (by boiling with a little free sulphuric acid until

all emulsion is destroyed ; the acids are then settled and washed with boiling water).

The Twitchell process is used largely in America and, to some extent, on the Continent, but does not appear to make very great headway in England. Its advantages are cheapness of reagents and low steam consumption combined with a concentration of glycerine in the aqueous liquors which approaches that of the autoclave process. *Per contra*, the hydrolysis is somewhat slow by comparison with the latter, and there is a tendency to the production of dark-coloured fatty acids.

M'Kee and Lewis [4] substitute *p*-cymene for naphthalene in the agent, and hold that this leads to less discoloration and more rapid action ; whilst the Vereinigte Chemische Werke [5] reach the same end by employing a similar product obtained by sulphonation of a mixture of naphthalene and hydrogenated castor-oil acids.

Theoretically, these agents are interesting in their close simulation of what may be supposed to be the essential structure of a typical hydrolytic enzyme (*cf.* Section III, Chapter V, p. 282).

Acid-hydrolysis of Fats.—If a completely dry neutral fat is intimately mixed with about 5–8 per cent. of 96 per cent. sulphuric acid and heated at 110°–120°, with mechanical agitation and admission of dry steam, for about eight to twelve hours, complete hydrolysis is effected. This result depends on the catalytic action of the mineral acid, which is mainly hydrolytic, but also partially that of a sulphonating agent (aliphatic sulphonic derivatives being produced and broken down by the elements of water into hydroxy-fatty acids and regenerated sulphuric acid).

As might be anticipated, the resulting fatty acids are extremely dark in colour, whilst much of the liberated glycerine is destroyed by the action of the sulphuric acid. It is therefore necessary to submit the crude fatty acids to purification by distillation

in a current of super-heated steam, and in practice, although used on quite a large scale, the process is applied in general only to low-grade fats, such as bone greases, etc., the glycerine in which is hardly worth recovery and the fatty acids from which, in any case, would require distillation in order to render their colour satisfactory.

Production of Benzaldehyde and Benzoic Acid from Chlorinated Toluene.

The process chiefly employed for the manufacture of benzaldehyde consists in chlorinating toluene, when a mixture of benzalchloride, $C_6H_5.CHCl_2$, with benzotrichloride, $C_6H_5.CCl_3$, is formed. If it is desired to obtain benzoic acid as main product, the chlorination is carried on until the toluene is transformed almost entirely into the trichloride.

Either chloride, when heated with aqueous caustic soda or milk of lime, passes into the corresponding hydroxylated compound :—

$$C_6H_5.CHCl_2 + H_2O = C_6H_5.CHO + 2HCl$$
$$C_6H_5.CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl,$$

but the conversion is slow unless the action is carried out above 100° (*i.e.*, under a moderately high pressure).

Schulze [6] found that the presence of metallic iron or iron salts accelerated the hydrolytic action of water—so much so that under these conditions rapid decomposition occurred at or below 100° ; the catalysed action is conducted as follows :—

(*a*) *Benzalchloride containing Benzotrichloride as By-product*.—Sixty parts of benzalchloride are gently warmed with 10–15 parts of water, and 0·02 parts of metallic iron in powder form (or of an organic salt of iron) are added, after which the mixture is heated to about 95°. Hydrolysis then sets in, and hydrochloric acid distils off and is absorbed in the usual way in a water-scrubber or tower ; when the process slows down, 9 parts of quicklime, slaked to a thin paste with water, are added and the liquor

is steam-distilled. Benzaldehyde passes over, and the residual liquor is worked up for calcium benzoate or benzoic acid.

(*b*) *Benzotrichloride*.—When benzoic acid is the main product, it is usual to add the alkali at the commencement of the operation, milk of lime from 34 parts of quicklime being used, whilst the proportions of the other reactants remain as in the first example.

This process is generally the cheapest source of benzaldehyde and benzoic acid, but the products, especially benzaldehyde, retain traces of chlorine compounds which make them unsuitable for use in edible products or high-grade perfumes. For most other purposes (*e.g.*, use in industrial synthetic operations) benzaldehyde and benzoic acid from chlorinated toluene are sufficiently pure.

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CHAPTER III

ESTERIFICATION AND DEHYDRATION OF ALCOHOLS BY MINERAL ACIDS

THIS group of processes—the elimination of the elements of water from an alcohol and an acid yielding an ester, or from an alcohol alone to give an ether or a hydrocarbon—is equal in technical importance to the hydrolytic actions which were reviewed in the preceding chapter. The theoretical principles of esterification were referred to in Section I. (pp. 54, 56), and it must suffice here to indicate the relationship of technical practice to theory. Thus it may be pointed out, in the first place, that in some cases it is possible to obtain efficient conversion of an alcohol to an ester solely by conforming to the law of mass action which, as Berthelot and St. Gilles [1] showed in 1862, controls the changes represented in the system

$$R.OH + R'COOH \rightleftharpoons R'COOR + H_2O$$

If it is possible to remove one of the components of this system continuously (*e.g.*, to withdraw water by evaporation) the process will tend to become complete in one or other direction. Thus, for example, glycol or glycerol, when heated with equivalent weights of higher fatty acids under reduced pressure, passes smoothly into the neutral fatty esters or synthetic fats (Schlinck,[2] Franck [3]); in such cases adequate conversion to ester is secured by employing conditions of temperature and pressure which ensure removal of water as fast as it is formed, without the intervention of a catalyst.

In many instances, however, one or more of the components of the system—alcohol, acid or ester—is appreciably volatile, and here recourse is frequently

had to the aid of catalysts, which may be either solids at the surface of which the gaseous alcohol and acid interact, or, as happens most frequently in technical practice, the catalytic esterification may proceed entirely in the liquid phase (*cf.* Section I., Chapter IV, pp. 54–59).

The catalysts employed in technical esterifications in the liquid phase are almost exclusively strong mineral acids, especially hydrochloric acid, sulphuric acid and phosphoric acid. Sulphuric acid probably antedates the others in its use in this connection, which extends back to the researches of Williamson [4] and even earlier ; its efficiency was formerly considered to be due to its affinity for water, but this view has been shown by Senderens and Aboulenc [5] (1911 and later), and by Bodroux [6] to be inadequate. These workers found that the presence of very small proportions (*e.g.*, 1 per cent.) of sulphuric acid, was capable of effecting very high conversions to ester in many cases, and that similar concentrations of anhydrous aluminium sulphate produced the same order of results, whereas an anhydrous neutral salt (*e.g.*, sodium sulphate) was ineffective. The action must, therefore, be ascribed to catalysis as opposed to the mere fixation of water by the agent employed. Many years ago, also, it was observed by Victor Meyer and Sudborough [7] that, in the preparation of organic esters, sulphuric acid could be replaced by a saturated solution of hydrogen chloride in the alcohol employed, esterification thus proceeding in due course at room temperatures ; at about the same time, Emil Fischer and Speier [8] introduced the use of an alcoholic solution containing about 0·5–1 per cent. of hydrogen chloride, rapid and relatively complete esterification being effected in many cases when organic acids were boiled under a reflux condenser with this agent for a relatively short time.

The choice of mineral acid in technical practice is determined by several considerations. Sulphuric acid

is somewhat cheaper, it is non-volatile, and therefore does not yield acid vapours (so that only the still portion of the plant comes in contact with mineral acid), and it is easily removed by washing the finished product with water; on the other hand, its charring and generally violent action may be inconvenient in the case of many organic compounds. Hydrochloric acid is perhaps not quite so efficient on the whole as sulphuric acid, and it passes to some extent into the vapour phase; yet it is milder in its general action on the more delicate organic derivatives and in many instances gives rise to a smaller or insignificant amount of undesired by-products.

The use of these agents will be illustrated by a brief description of the industrial preparation of some typical esters, acetals, ethers and olefines.

Esters.—Many esters have technical importance as solvents, perfumes (including "fixatives"), medicines and, lately, as textiles (cellulose acetates). We are concerned here solely with the extent to which their manufacture involves homogeneous catalysis, and the discussion will be oriented primarily with respect to the methods adopted. The acetates form a large and important section of the industrially useful esters, and afford a suitable background upon which to illustrate the application of several catalytic processes.

Ethyl Acetate.—This is one of the most important esters used in industry, both as a solvent and in other ways. Several alternative processes exist for its manufacture, and it should first be recalled that modern practice utilises acetaldehyde as the raw material (*cf.* p. 296), the aldehyde being "polymerised" to ethyl acetate by aluminium ethylate, a reaction first noticed by Petrenko-Kritschenko;[9] as already indicated in Chapter I. of this section, this method is quite possibly destined to supersede the other esterification processes based on alcohol and acetic acid.

(Here it may be mentioned that an analogous catalytic transformation[10] of an aldehyde to a corre-

sponding ester is used in practice for the manufacture of the perfume (artificial musk solvent) *benzyl benzoate* : 100 parts of benzaldehyde are heated to about 110° and stirred thoroughly whilst a hot solution of 1 part of sodium in 20 parts of benzyl alcohol is added. A vigorous action occurs, which may be summed up as

$$2C_6H_5.CHO = C_6H_5.COO.CH_2.C_6H_5.$$

The product is recovered by steam-distillation, after acidification of the diluted mass with dilute acid, followed by fractional distillation to eliminate the free benzyl alcohol present).

Older methods of production of ethyl acetate include the heating and subsequent distillation of acetic acid with some excess of ethyl alcohol in presence of hydrochloric acid, anhydrous calcium chloride or, more frequently, sulphuric acid in amount equal to not more than 5 per cent. of the interactants. Aromatic sulphonic acids, especially naphthalene-β-sulphonic acid, have also been employed as catalysts of esterification, but probably sulphuric acid is used to a much greater extent than any of the other substances. When operating on the intermittent system a first distillate of ethyl acetate, alcohol, water and some acetic acid is obtained, the sulphuric acid being usually run to waste ; the crude ester is washed with carbonate solution and distilled over calcium chloride in order to free it from both alcohol and water. Comparatively recently, Backhaus,[11] Durrans[12] and others have patented plant for the continuous production of ethyl acetate by the sulphuric acid method, the general scheme being to cause a pre-heated mixture of alcohol and acetic acid with about 3 per cent. of sulphuric acid to enter and flow down the lower part of a fractionating column. The esterified mixture passes up the column through plates of the usual type, and ethyl acetate containing some alcohol is recovered from the top and subjected to further purification as required.

The sulphuric acid method (employing from 3–5

per cent. of the acid in the reaction mixture) is similarly used in the preparation of the following esters from their constituent alcohols and acids :—

Amyl acetate (solvent),
Methyl and amyl salicylates (perfumes and medicines),
Benzyl and bornyl acetates (perfumes),
Methyl and ethyl benzoates (perfumes),
Ethyl succinate (fixative for perfumes).

The details of procedure vary with the compounds in question : thus, if the alcohol is more expensive than the acid and is of similar boiling point to the ester (as often happens), an excess of acid instead of alcohol is employed. The temperature of treatment also varies : thus, whilst the more volatile compounds are refluxed and finally distilled direct from the reaction mixture, in other cases (*e.g.*, methyl salicylate), the process is undertaken at about 100°–120°, followed either by removal of the (relatively high-boiling) product under diminished pressure or by preliminary removal of the mineral acid by washing with water, distillation being subsequently carried out. In a few instances (*e.g.*, bornyl acetate) the esterification is carried on at quite a low temperature in order to avoid undesired side reactions.

It has already been mentioned that sometimes the use of sulphuric acid is quite inadmissible owing to its destructive action on the organic compounds present, and that in such cases, following the Fischer-Speier method, anhydrous hydrogen chloride is used in technical practice. This is well illustrated by the perfume fixatives *ethyl succinate*, *ethyl citrate* and *ethyl lactate* : whilst the first of these may be prepared by refluxing 10 parts of succinic acid with 15 parts of alcohol in presence of 0·5 parts of sulphuric acid, distilling off the excess of alcohol, cooling, diluting with water, neutralising, and fractionating the neutral ester, the last two are best manufactured by passing

dry hydrogen chloride into solutions of the acids in a similar excess of alcohol, standing or heating at about 50° for twelve to twenty-four hours and distilling under reduced pressure after removal of the free hydrochloric acid.

Other examples in which the hydrochloric acid method is preferable are those of *methyl* and *ethyl cinnamates* and of *methyl anthranilate*, each of which is important in perfumery.

Acetylations with Acetic Anhydride or Acetyl Chloride.—In yet other instances, the use of any mineral acid is inapplicable owing to the ready isomerisation of the alcohol present under these conditions; this obtains especially in the case of terpene alcohols, such as geraniol, linalool and menthol, the acetates of which are in demand in perfumery. Further, the hydroxyl groups of phenols, of cellulose, and some other compounds are not readily esterified by organic acids in presence of mineral acid catalysts. In both these cases recourse is usually had to acetic anhydride (or, less frequently, acetyl chloride) in order to introduce the acidic radicle.

It is well known that the acetylating action of acetic anhydride proceeds more rapidly, and at a lower temperature, in presence of a small proportion of anhydrous sodium acetate, or of anhydrous zinc chloride. The mechanism of the intervention of these materials, although not precisely understood, is undoubtedly catalytic in nature, and these processes fall within the group of esterification methods now under review. They are used technically, for example, in the production of *acetates of linalool, menthol and geraniol and of acetylsalicylic acid* (aspirin, *cf.* below). Thus a mixture of 5 parts of linalool or geraniol, 3 parts of acetic anhydride and 1 part of anhydrous sodium acetate may be well stirred at 100°–110° for some hours, and then worked up by decomposition of unchanged anhydride with water followed by fractionation under reduced pressure in the usual manner.

Less frequently acetyl chloride is used as acetylating agent in the cold in presence of pyridine. This procedure, more familiar in the laboratory in the case of benzoylation, is, however, not catalytic, since the function of the tertiary base present is to fix the hydrogen chloride liberated in chemical combination, and an excess of the base is usually employed.

Finally, it should be mentioned that in one or two notable industrial processes of acetylation, the action is catalysed by sulphuric acid, although, in order to effect complete acetylation, it is necessary to employ a certain amount of acetic anhydride in admixture with acetic acid. This statement applies to the preparation of acetylsalicylic acid and of cellulose acetates.

Acetylsalicylic Acid (*Aspirin*).—In addition to non-catalytic methods of manufacture, the use of acetic anhydride assisted by sulphuric acid is widely practised. One hundred and thirty-eight kilograms of salicylic acid are dissolved in 120 kg. of acetic anhydride containing 0·5 kg. of concentrated sulphuric acid and heated at 50°–60° for some time, finally increasing the temperature to 90°. The product is cooled to 0° with agitation, and separated acetylsalicylic acid is filtered off and washed with water at 0°, and later with toluol. The filtrates and washings are worked up for acetic acid, unchanged acetic anhydride and unchanged salicylic acid, whilst the acetylsalicylic acid is purified by recrystallisation.

Cellulose Acetates.—The acetylation of cellulose has, of course, developed of late years into a very large industry, and a full description of the technique of the various patented processes at present used is beyond the scope of the present work. The rate of acetylation and the character of the products obtained depends greatly on the purity of the original cellulose fibre, its moisture-content, whether it consists of cellulose or hydrated celluloses (" hydrocelluloses " produced by preliminary maceration with dilute mineral

acid), and the manner and order in which it is mixed with the acetylating agents.

The cotton or other fibre is first of all degreased by treatment with petrol or benzol, and may then be partially hydrated by steeping in dilute sulphuric acid,[13] although, whilst facilitating acetylation, this weakens the fibre to some extent. Finally it is dried as thoroughly as possible (to a moisture content not exceeding 2–3 per cent.).

Two examples from patent literature may be given to illustrate the influence of conditions of acetylation on the product obtained.

(*a*)[14] A mixture of 270–310 parts of acetic anhydride, 390–410 parts of acetic acid, and 5–8 parts of sulphuric acid is added to 100 parts of cellulose with good stirring and cooling so that the temperature does not rise above 40°, although finally it is raised to about 55°. The action is continued until the product is completely soluble in chloroform, when it is precipitated with water, freed from acetic acid, and then consists mainly of the triacetate of cellulose.

(*b*)[15] One hundred parts of cellulose are added to a mixture of 800 parts of glacial acetic acid, 200–350 parts of acetic anhydride, and 15–20 parts of sulphuric acid maintained at 0°. The acetylation is carried out at a low temperature and requires about three to six hours, the temperature being allowed to rise to 30° towards the end of the period. The greater proportion of acetic acid present is stated to retard undue disruption of the cellulose structure and result in products of greater viscosity and tensile strength.

In nearly all processes for acetylation of cellulose the catalyst employed is sulphuric acid ; hydrochloric acid has also been proposed, but does not appear to be so useful as the former acid, whilst zinc chloride is recommended as an acetylating catalyst on the score that its action is more regular and less disruptive than that of sulphuric acid.

It will be noticed that, from the catalytic standpoint,

technical experience in the acetylcellulose industry is broadly similar to that in the manufacture of esters, the cheap and convenient sulphuric acid being employed under appropriate conditions whenever possible, whilst for special cases other catalysts (in this instance zinc chloride) are used.

Acetals.—The acetals are mixed ethers derived from an alcohol and the aldehydrol form of an aldehyde, $R.CH(OR')_2$; in one or two instances they are of therapeutic value and are manufactured by condensation methods which involve homogeneous catalysis similar to that dealt with in the production of esters.

Methylal, $CH_2(OCH_3)_2$, (b.p. 42°), the dimethyl ether of formaldehyde, is used as an anæsthetic and is produced by heating 2 parts of paraformaldehyde with 5 parts of a 1 per cent. solution of hydrogen chloride in methyl alcohol at 40°–50° under a reflux condenser for some hours. After standing for some time and cooling, sufficient lime is added to neutralise the mineral acid and the liquid is fractionated.

Acetal, $CH_3.CH(OC_2H_5)_2$, (b.p. 104°), is the corresponding diethyl ether of acetaldehyde, and is produced from acetaldehyde and alcohol by the above method or by treating a mixture of acetaldehyde and alcohol with about 10 per cent. of its weight of calcium or similar chloride in presence of a small amount of hydrochloric acid under a reflux condenser.[16]

The action of hydrochloric acid or calcium chloride in the formation of acetals is essentially one of catalytic dehydration, according to the scheme

$$\left\{\begin{array}{l} R.CHO + H_2O \longrightarrow R.CH(OH)_2 \\ R.CH(OH)_2 + 2R'OH \longrightarrow R.CH(OR')_2 + H_2O. \end{array}\right.$$

Ether.—A very important type of catalytic dehydration in the liquid state is the removal of the elements of water from two molecules of an alcohol, forming the corresponding ether.

Ethyl Ether, $(C_2H_5)_2O$, is, of course, used in very large quantities in surgery as an anæsthetic, and in chemical work and in fine chemical manufactures as

a solvent. It was also required extensively during the late war in the manufacture of propellant explosives, when it was found that a mixture of ether and alcohol was a serviceable substitute for acetone as a solvent for nitro-cellulose and nitroglycerine. A similar mixture, under the name of Natalite, has been found useful as a fuel for motors, and is capable of being used in engines designed for the combustion of petrol.

For industrial purposes, ether has always been produced by the catalytic action of sulphuric acid on alcohol, known and represented for years past as due to the sequence of actions

$$\begin{cases} C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O \\ C_2H_5.HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4. \end{cases}$$

By reason of this procedure, the anæsthetic is frequently sold as "sulphuric ether," whilst the equally familiar "methylated ether" is the product from methylated or denatured alcohol, and contains a small proportion of methylethyl ether and possibly dissolved dimethyl ether.

Prior to the war period the production of ether was effected by a discontinuous process: four parts of alcohol and three parts of sulphuric acid were heated in a lead-lined still to about 140°, when ether commenced to be formed and a distillate of ether mixed with alcohol was collected. Further quantities of alcohol were added to the still to replace the distillate until the amount of water retained by the sulphuric acid was great enough to retard the dehydration. The remaining alcohol and ether were then distilled off and the ether and alcohol separated by fractionation, the recovered alcohol being collected and used with a fresh charge of sulphuric acid. Senderens [17] showed that, as in the case of esterification (*cf.* p. 321), the process could be increased in efficiency and conducted at a lower temperature (about 120°–130°) if a small percentage of anhydrous aluminium sulphate were added to the still-charge. Nevertheless the

discontinuous process involved considerable losses of alcohol and also of sulphuric acid, and was also wasteful from the point of view of heat consumption.

For the production of ether for ether-alcohol mixtures in explosives and internal combustion engine fuel, a continuous process was devised by Barbet,[18] the first English installation being at H.M. Factory, Gretna. The plant consists essentially of the following parts :—

(i.) An alcohol vaporiser, comprising a steel vessel fitted with vertical steel tubes ;

(ii.) The reaction still, constructed of lead-lined steel ;

(iii.) A continuous fractionating and rectifying column, built in copper and made up of two sections, the lower one serving to recover unchanged alcohol and containing twenty-two fractionating plates, whilst the upper one (one-third the height of the former and somewhat narrower) is designed to rectify the ether. The two parts of the column are separated by a solid plate, and vapour from the top of the lower column passes to the lowest plate of the upper part through an intermediate condenser, which returns a continuous stream of alcohol to the top plate of the lower column. Alcohol is recovered from a plate near the top of the lower column and ether is similarly withdrawn from the top plates of the upper section and, to a certain extent, by condensation of the vapours in condensers attached to the head of the column.

In starting up the process a mixture of one volume of 78 per cent. sulphuric acid and two volumes of 92 per cent. alcohol is charged into the still and heated, whilst alcohol is fed into the alcohol vaporiser and, when the contents of the still are at 105°, is admitted in the state of vapour into the still. The temperature of the latter is increased, and finally, as the reaction increases, steam is shut off and the temperature of reaction (128°) maintained by the heat evolved, sufficient alcohol vapour being blown into the acid

mixture to maintain it at about this point. The process is thereafter continuous, and the plant will run for long periods before it is necessary to use fresh acid.

The vapours from the still pass through a 2 per cent. solution of caustic soda in a scrubber, and thence into the lower fractionating column (about half-way up). This column is supplied with live steam at its base and is so controlled that the effluent at its base does not contain any alcohol. The mixture of ether and alcohol is driven up the column by the steam as indicated above and separated into its components, anhydrous alcohol containing a small percentage of ether being withdrawn from the top of the lower column and pure ether separated at the top of the upper column.

A unit capable of producing 25 tons per 24-hour day gave an overall efficiency (yield) of ether of over 94 per cent. on a continuous production of 5,000 tons, the materials consumed per ton of ether being 1·43 tons of 92 per cent. alcohol, 0·0012 tons of 100 per cent. sulphuric acid, and 0·0014 tons of caustic soda. The weight of steam used varied between 6,000 and 10,000 lb. per ton of ether, according to whether fresh or recovered alcohol was used in the still. The efficiency and smoothness of this continuous system of ether production renders it an excellent example of the possibilities of catalysis in industrial organic chemistry, and for this reason the Barbet process has been described at considerable length.

Ethylene.—The trend of economic factors seems to lie in the direction of converting ethylene into alcohol (*cf.* this section, Chapter I., p. 303) rather than to demand the production of ethylene from alcohol, but it sometimes happens that the hydrocarbon is required. Dehydration of alcohol with production of ethylene can be effected catalytically by several means; the passage of heated alcohol vapour over appropriate

solid catalysts has been dealt with in Section II. (Chapter VIII, p. 188), but older methods consist in catalytic dehydration in a homogeneous liquid system by means of sulphuric or phosphoric acid.

If, in the process described above for the discontinuous preparation of ether, the temperature of the charge in the still is raised to about 160°–170° and the proportion of alcohol reduced, ethylene is produced instead of ether :—

$$\left\{\begin{array}{l} C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O \\ C_2H_5.HSO_4 = C_2H_4 + H_2SO_4. \end{array}\right.$$

For ethylene production the ratio of alcohol to concentrated sulphuric acid in the still is kept at about one of alcohol to two of acid (by volume) ; as in the case of ether, the action proceeds more rapidly and readily if the charge contains 5 per cent. of anhydrous aluminium sulphate : at 157° the evolution of ethylene is more than twelve times as rapid in presence of the aluminium salt as when sulphuric acid only is used.

The use of sulphuric acid at the necessary temperature leads to a certain amount of carbonisation with concurrent production of sulphur dioxide, and, especially for relatively small outputs of ethylene, it is more economical and convenient to employ phosphoric acid. For this purpose metaphosphoric acid (" syrupy phosphoric acid ") is charged into a lead-lined still, connected with a condenser or scrubber followed by a gas-holder for the ethylene, and is heated to about 150°, when alcohol is slowly added so that a steady and continuous evolution of ethylene takes place. In this way a more or less continuous production of relatively pure ethylene is secured.

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CHAPTER IV

EXAMPLES OF OTHER HOMOGENEOUS CATALYTIC ACTIONS EMPLOYED IN THE ORGANIC CHEMICAL INDUSTRIES

THE types of homogeneous catalysis which have so far been described, fall, in some measure, into a series of connected stories, but there is left a wider number of processes, in common use in the dyestuffs and other organic chemical industries, which depend upon catalytic action for their efficiency; in practically all these cases, also, the application of catalysts has grown up more or less fortuitously and rests on isolated discoveries which, however logically developed in their later stages, were by no means the result of any definite attempt to apply catalysis to the processes in question.

Consequently systematic treatment of this diffuse field is extraordinarily difficult, whilst it is impossible to discuss at length in this volume the technical procedure involved in any given case. Nevertheless, in the glamour of modern thermodynamical treatment of catalysis and the splendour of the recent developments in the fields of high-pressure catalytic synthesis, fat and naphthalene hydrogenation, the catalytic syntheses from acetylene, and so on, it is apt to be overlooked that for upwards of half a century catalytic processes have been widely used as a matter of course in the technical chemistry of the aromatic derivatives. The reason for this may lie in the frequent comparative obscurity of the function of the catalyst, or in the fact that the latter magic word was not in such demand when many of these processes were in their infancy. However this may be, it seems reasonable in a treatise on industrial catalysis to attempt a review of these older forms of

catalytic action, even though this is confined almost to a bare enumeration of a large number of somewhat divergent chemical actions.

Since most of the actions under consideration are conducted in a homogeneous liquid condition, it is convenient to deal with them in this chapter, including, at the same time, a minority of similar processes which may, strictly speaking, involve catalysis at a solid surface, and therefore may belong more correctly to one or other of the chapters of Section II. It is only possible to indicate the scope of this part of the subject by reference to a few general cases selected from the many which are available ; these are classified under the general headings of the types of organic reaction to which they belong.

(a) Actions of Condensation.

One or two cases, which resemble those discussed in the last chapter in that the actions involve the elimination of the elements of water from two molecules of organic compounds, will first receive mention. A very useful synthetic laboratory process, which also has some industrial importance, is the condensation of an aldehyde or ketone with acetone according to the scheme

$$R.CHO + CH_3.CO.CH_3 = R.CH : CH.CO.CH_3 + H_2O.$$

This proceeds, as originally shown by Claisen,[1] in a dilute alkaline medium, the action of the alkali being catalytic.

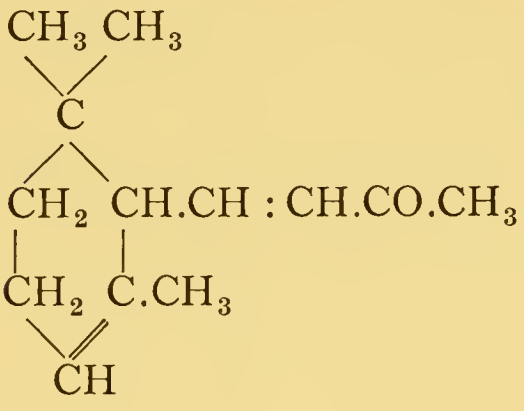
The resulting unsaturated ketones have, as a rule, no technical interest, but in some cases they are convertible into derivatives of industrial value.

Thus, Tiemann and Krüger [2] found that baryta solution caused citral to condense with acetone to give the compound *pseudo-ionone*

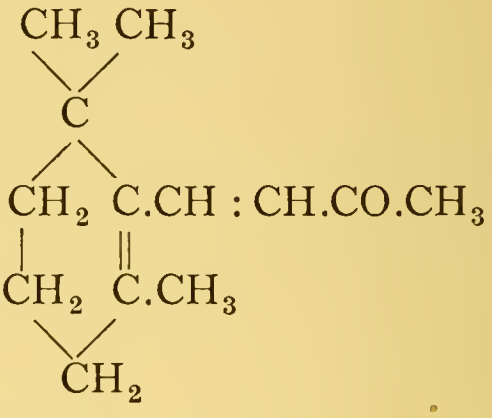
$$(CH_3)_2C : CH.CH_2.CH_2.C(CH_3) : CH.CH : CH.CO.CH_3$$

which, by the further catalytic action of dilute sul-

phuric acid, is rearranged into a mixture of isomeric ring-compounds, the *ionones* :—

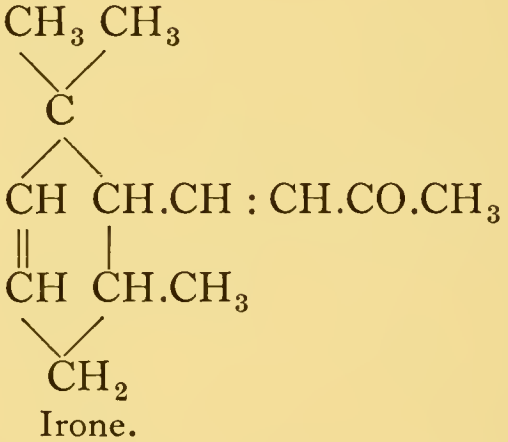


α-Ionone.



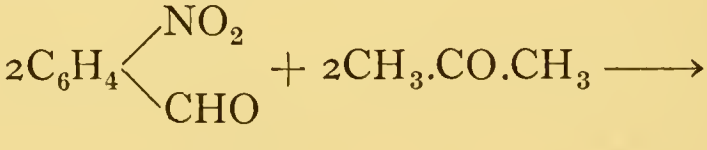
β-Ionone.

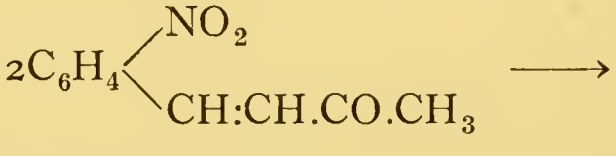
These are produced in large quantities for the sake of their perfume, which closely resembles that of violets or orris, due, in the latter case, to the presence of yet another ketone isomeric with the ionones, namely,

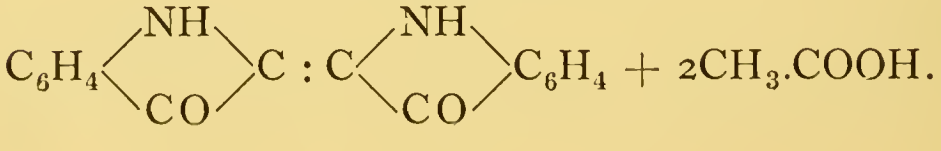


Irone.

Again, in Baeyer and Drewsen's [3] process for the manufacture of synthetic indigo, *o*-nitrobenzaldehyde is similarly condensed with acetone by means of dilute caustic soda, further rearrangement leading to the formation of indigo :—







Finally, the very modern industry of plastic and moulded products and lacquers from the fusible or infusible resins (bakelite, etc.) depends on the controlled condensation of phenols with formaldehyde,[4] which is assisted by means of very feebly alkaline catalysts. The most commonly used are ammonia and hexamethylenetetramine, but other amines, amides and even mildly alkaline salts or hydroxides of the alkali and alkaline earth metals are available, as shown by the published results of Baekeland. The proportion of alkali employed is always less than 20 per cent. of that necessary for the theoretical formation of a phenolic salt with the added base.

The next class of condensations to which we shall refer are those in which hydrochloric acid is eliminated from two organic molecules by Friedel and Crafts' classical aluminium chloride method.[5] This is of especial interest because it is one of the few of the older organic catalyses which have been studied with reference to reaction-mechanism. It is also an instance in which the intermediate complex between catalyst and either interactant is sufficiently stable to be isolated: crystalline derivatives of the form $(RCl, AlCl_3)_2$ have been isolated in the case of acid chlorides, and double compounds such as $(C_6H_6, AlCl_3)_2$ from hydrocarbons and aluminium chloride. In a thorough study of the interaction of toluene and benzyl chloride in presence of anhydrous aluminium or ferric chlorides, Steele[6] found in 1903 that a short period of induction marked the formation of the intermediate derivative, after which, broadly speaking, the action proceeded according to the unimolecular law and declined in speed as the concentration of organic halogen compound diminished; after a time the influence of a complex made up of the product and the catalyst served as an additional retardation. It appears that Steele's results form a close analogy to the views developed some fifteen years later, when very similar deductions were made with regard to the

probable mechanism of the addition of hydrogen to unsaturated liquid organic compounds in presence of nickel.

The application of the Friedel-Craft synthesis in industry is widespread ; a cursory indication of some of the variants may be given. An interesting recent suggestion for the production of toluene from benzene is due to Sifton,[7] who employs iron turnings in admixture with anhydrous aluminium chloride. Hydrogen chloride (mainly derived from that subsequently expelled in the synthesis) is dried and passed through stills containing methyl alcohol and anhydrous zinc chloride, when gaseous methyl chloride is produced, freed from contained methyl alcohol in condensers, and passed up a series of plate-columns. The plates contain layers of the catalyst over which benzene circulates in a downward direction, the columns being maintained at 45–55°. The plant is operated on the counter-current system, so that the fresh methyl chloride enters a column in which the benzene is already nearly converted into toluene and emerges through one containing almost fresh benzene.

The synthesis is more widely applied technically in the preparation of aromatic ketones and allied derivatives, and very frequently the organic halide consists of carbonyl chloride, $COCl_2$. Thus, when 40 parts of dimethylaniline and 6 parts of carbonyl chloride are maintained at 20°–30° for some hours in presence of 10 parts of aluminium (or ferric) chloride, the dyestuff Crystal Violet is produced in good yield [8] :—

$$\begin{cases} 2\ C_6H_5.NMe_2 + COCl_2 \longrightarrow \\ \qquad Me_2N.C_6H_4.CO.C_6H_4.NMe_2,\ 2HCl \\ (Me_2N.C_6H_4)_2.CO\ ,\ 2HCl + C_6H_5.NMe_2 \longrightarrow \\ \qquad (Me_2N.C_6H_4)_2C : C_6H_4 : NMe_2Cl + H_2O + HCl. \end{cases}$$

A nearly related process to the last is the Gattermann synthesis [9] of aldehydes from carbon monoxide, hydrogen chloride and an aromatic hydrocarbon in presence of aluminium chloride containing about

10 per cent. of cuprous chloride ; the mixed gases are passed through dry benzene containing a considerable proportion of the catalyst at about 40°, when the following action occurs :—

$$C_6H_6 + CO\ (+ HCl) = C_6H_5.CHO\ (+ HCl).$$

Hoesch improved this process subsequently by substituting hydrocyanic acid for the carbon monoxide :

$$C_6H_6 + HCN\ (+ HCl) = C_6H_5.CH : NH\ (+ HCl),$$

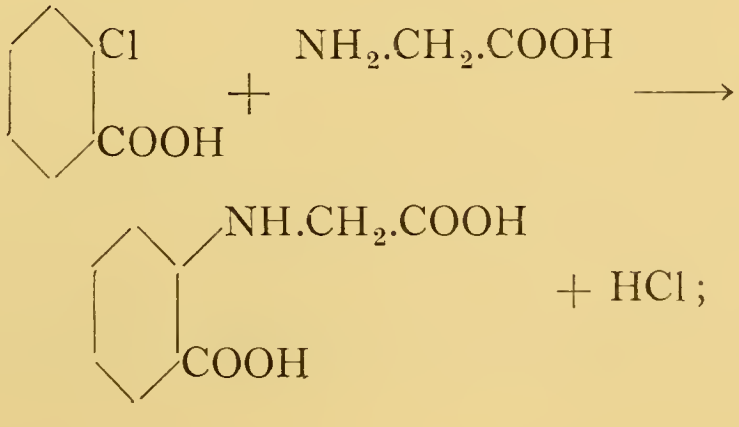
the imino-aldehyde being readily converted into the aldehyde by the action of water ; this modification has been found useful in technical practice, especially in the production of aldehydic derivatives of phenolic ethers, *e.g.*, that of vanillin from guaiacol.

Cuprous chloride and other cuprous salts have also proved serviceable in the conversion of aromatic diazo-compounds into chloro-, bromo-, or other derivatives by the well-known Sandmeyer reaction [10] :—

$$R.N : N.Cl + Cu_2X_2 \longrightarrow RX + N_2 + Cu_2XCl.$$

Gattermann's modification [11] of this process, in which finely-divided metallic copper is used in place of the cuprous halide, may be a case of heterogeneous catalysis, or the change may be effected in reality by traces of cuprous salt produced in the reaction medium from the metal.

The Gattermann copper catalyst also effectively promotes the elimination of hydrogen chloride between a chlorophenyl residue and an amino-group in some cases ; for example, in an important stage of one form of the phenylglycine indigo synthesis [12] :—



it is similarly useful in the production of nitraniline derivatives by the action of ammonia on chloro-derivatives of nitrated hydrocarbons.

(b) Formation of Hydrocarbon Halides by Substitution or Addition.

Technical chlorinations are frequently facilitated by the presence of metallic or other chlorides which act as "chlorine carriers" or catalysts. Some of the more important applications of these catalysts are as follows :—

(i.) Benzene and toluene are converted into chloro-derivatives by passing a current of dry chlorine gas into the hydrocarbon, which contains in suspension either anhydrous ferric chloride, or a mixture of the latter with reduced iron powder (equivalent to ferrous chloride or subchloride).[13]

(ii.) In chlorination of the aliphatic radicle in an aromatic hydrocarbon, for example, in the production of benzyl and benzal chloride from toluene, phosphorus trichloride is a useful catalyst, and probably sulphur chloride is also efficient. The action in this case is carried out at the boiling-point of the liquid mixture in presence of 1–3 per cent. of phosphorus trichloride ; the main product is the monochlorinated derivative (benzyl chloride) unless the action of the chlorine is very prolonged or carried out in strong ultra-violet light.

(iii.) Similarly, substitution of hydrogen by chlorine in the methyl radicle of acetic acid is facilitated by the presence of small quantities of sulphur or phosphorus (Russanoff).[14] Monochloracetic acid is produced by passing chlorine gas into boiling glacial acetic acid containing about 1 per cent. of finely-divided sulphur for some hours ; chlorides of sulphur are formed initially and chlorination then proceeds steadily and almost quantitatively.

(iv.) Addition of halogen is not so widely practised technically as substitution, but an important example

consists in the addition of chlorine to acetylene,[15] which is hardly safe on the large scale, except when aided by catalytic action. Whilst iron, aluminium, or sulphur chlorides are stated to be useful for this purpose, the most suitable compound is antimony pentachloride, which forms moderately stable addition compounds with both dichloroethylene CHCl : CHCl and tetrachlorethane $CHCl_2.CHCl_2$.

Tetrachlorethane has useful properties as a solvent, etc., but is surpassed by trichloroethylene, $CHCl : CCl_2$ (Westrosol), in solvent power, stability and convenience of boiling-point. Fortunately the latter compound can be obtained in over 80 per cent. yield when tetrachlorethane (100 parts) is heated with slaked lime (60 parts) and water (50 parts), and it is manufactured by this means on an extensive scale. The tetrachlorethane is manufactured by passing acetylene and chlorine alternately into a solution of antimony pentachloride in the product itself. In the first phase, the tetrachlorethane is converted into dichlorethylene :—

$$(CHCl_2.CHCl_2 , SbCl_5) + C_2H_2 \longrightarrow (CHCl : CHCl, SbCl_5) + CHCl : CHCl,$$

whilst subsequently the latter compound is re-converted into tetrachlorethane :—

$$(CHCl : CHCl , SbCl_5) + Cl_2 \longrightarrow (CHCl_2.CHCl_2, SbCl_5).$$

At suitable intervals the passage of gas is suspended whilst the tetrachlorethane produced is removed by fractional distillation. By this means acetylene and chlorine are never actually brought into contact in the free condition, and a somewhat dangerous process becomes quite safe.

(c) Actions of Oxidation.

Four typical processes may be selected from a large number in order to illustrate the technical applications of catalytic action in the oxidation of organic derivatives in the liquid condition, as distinct

from the gaseous oxidations dealt with in Section II., Chapters VII and VIII (pp. 175 and 199).

(i.) An important use of oxidising catalysts is the addition of lead, manganese or cobalt " driers " to linseed and other oils which are to form the basis of paints and varnishes, or of linoleum or other oxidised fatty-oil products. Modern driers consist of salts of one or more of these metals with linoleic acid (unsaturated fatty acid) or abietic acid (rosin acids), whilst formerly the practice was simply to add to the heated oil a mixture of the oxides, or frequently lead oxide alone. The amount of metallic oxide present is greater in the older process than in the modern method.

The highly unsaturated glycerides of linseed and similar oils absorb oxygen on simple exposure to air, but at first very slowly (*i.e.*, there is a marked " period of induction ") ; the initial oxygen addition-product, however, acts as an excellent catalyst for further addition of oxygen, which then proceeds more rapidly and steadily. The function of the metallic salt " driers " consist in eliminating the induction period and rendering possible a free absorption of oxygen from the commencement.

The structure of the oxidised glycerides, which are generically termed " linoxyn," is complex ; a fuller description than space permits here, both of the abundant studies of the mechanism of oxidation of the drying oils and of their technical manipulation, may be found in the works to which reference is made in the bibliography to this chapter.[16]

(ii.) Toluene can be converted into benzaldehyde by oxidation with precipitated manganese dioxide in presence of moderately concentrated sulphuric acid. Appelbaum[17] finds that the oxidation is accelerated by the addition of a small proportion of ceric or ferric sulphate, and has patented an apparatus for the continuous production of benzaldehyde by this means, the benzaldehyde and toluene being

removed by steam, and unchanged toluene fractionated and returned continuously to the charge in the reaction-vessel.

(iii.) Aniline Black, the important dyestuff produced by oxidation of aniline, is conveniently prepared by treating a solution of aniline hydrochloride in water at ordinary temperatures with the theoretical amount of sodium chlorate, if small quantities of salts of certain metals are also present.[18] For this purpose vanadium or osmium compounds are the most active, whilst cerium salts or copper sulphate are also effective.

(iv.) Mercuric salts are frequently useful catalysts in oxidation processes, especially when the oxidation is effected by sulphuric acid (which is reduced to sulphur dioxide). The usual commercial method of manufacture of phthalic anhydride from naphthalene, for example, consists in heating the hydrocarbon with sulphuric acid at 250° or above in presence of about 1 per cent. of mercuric sulphate. The mercury salt increases the rate of oxidation very markedly, and, in consequence, minimises the production of sulphonated derivatives and other by-products. This example is well known as one of those instances in which the discovery of the catalytic method (in 1896) was fortuitous, the acceleration having first been observed owing to the accidental breakage of a thermometer in a batch of naphthalene which was being oxidised by sulphuric acid alone.[19]

(d) Catalysis in the Preparation of Organic Sulphur Compounds.

(i.) *Sulphonations.*—Mercuric sulphate is also useful in directing the course of sulphonation of the more complex aromatic hydrocarbons and derivatives. Thus, in presence of about 0·5 per cent. of this salt, anthraquinone yields a mixture of 1:5– and 1:8–anthraquinone disulphonic acids (α–substituted), whereas, in its absence, the products are the β–substituents, 2:6– and 2:7–anthraquinone disulphonic acids.[20]

Again, in the α-substituted sulphonic acids the sulphonic acid group can be replaced by hydrogen, in many cases, by boiling with dilute sulphuric acid, if mercuric sulphate is also present.[21]

(ii.) *Thio-compounds*.—Catalytic action is prominent in many of the reactions of organic compounds containing bi- and quadri-valent sulphur, and although many of these are not much used at present in technology, it would appear that their importance may increase in the near future, especially in connection with problems associated with the vulcanisation of rubber.

Thus iodine (or hydriodic acid) has an appreciable accelerating influence on the production of certain polythioderivatives,[22] *e.g.*, in the action

$$2R.SO_2H \text{ (sulphinic acid)} \longrightarrow R.SO_2.S.R \text{ (disulphoxide)} + H_2O + O,$$

and also in some cases of sulphonation [23] (*e.g.*, benzenesulphonic acid).

Again, copper, or salts of copper, exert an effect [24] on the condensation of aromatic chloro-derivatives with alkali sulphides or hydrosulphides of a similar nature to that mentioned above (p. 340) in the action of ammonia on chloro-derivatives ; sodium *o*-chlorbenzoate, heated at 150–250° with twice its weight of potassium hydrosulphide in presence of about 0·1 per cent. of precipitated copper, passes smoothly into sodium thiosalicylate :—

$$C_6H_4\begin{cases}Cl\\COONa\end{cases} + KHS = C_6H_4\begin{cases}SH\\COONa\end{cases} + KCl.$$

(iii.) *Accelerators in the Vulcanisation of Rubber*.[25] —The combination of sulphur with caoutchouc to form the resilient commercial product may be effected by mastication and heat-treatment with sulphur, or by alternate exposure of the rubber in solution to sulphuretted hydrogen and sulphur dioxide by the Peachey process. In either case the progress of the vulcanisation is aided to a marked extent if a fractional

percentage amount of one or other of numerous compounds known as " rubber accelerators " is present. The theoretical significance of what takes place in the vulcanisation, and of the exact function of the accelerator, is not yet clear, and it is natural, therefore, that the quest for accelerating catalysts should still remain to a certain extent empirical. The literature of the subject is very large, and dozens of new accelerators of improved and other types are patented every year ; reference should be made to the Reports of the Progress of Applied Chemistry issued annually by the Society of Chemical Industry, whilst the list of papers given at the end of this chapter [25] will afford a reliable guide to the main lines on which enquiry has been conducted in the past few years.

The utility of accelerators has been known since the earliest days of vulcanisation, when it was observed that mild alkalies, such as magnesia, lime or litharge, and also the proteins present in raw rubber, increased the speed of vulcanisation. The modern forms of accelerators, however, date from about 1913, when Bayer and Co.[26] patented the use of organic bases with a dissociation constant greater than 1×10^{-8} (*e.g.*, piperidine, benzylamine, *p*-phenylenediamine, etc.). These can be used at a concentration of 0·5 per cent. or less, whereas the amount of inorganic base employed was usually at least ten times this proportion.

As indicated, the investigations on organic rubber accelerators have been increasingly numerous since this date, and classes of compounds other than organic bases have been proved to be very serviceable. The chief general types of compound so far noted as efficient catalysts for this purpose include :—

(*a*) Organic bases of the type of piperidine ;
(*b*) Nitroso-compounds of the type of nitroso-dimethylaniline ;
(*c*) Diphenylguanidine and other substituted guanidines ;

(*d*) Thiourea and substituted thiocarbanilides; arylthiazoles, especially in the form of mercapto-derivatives;

(*e*) Zinc or lead salts of dialkyldithiocarbamic acids, or of dithiobenzoic acid;

(*f*) Condensation-products formed between two of the classes: organic base, nitroso-derivative, thio-compounds.

Whether all these variants are necessary, or which, if any, is the most efficient, does not appear yet to be decided. The object in view is to secure maximum rapidity of vulcanisation with no accompanying undesired side-effects, and with the minimum addition of accelerating catalyst. The importance of this aspect of the rubber industry may be judged (bearing in mind that the average proportion of organic accelerator present does not reach 0·5 per cent.) by the fact that, in 1923, the annual world consumption of synthetic accelerators for rubber was estimated at over 2,000 tons.

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